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# USSR Report

## CHEMISTRY

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25 June 1984

## USSR REPORT

## CHEMISTRY

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AEROSOLS

UDC 621.359.4-036.5

ELECTROFILTERS FROM POLYMER MATERIALS

Moscow KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 2, Feb 84  
pp 16-17

MOSHKIN, A. A., LOSOTO, A. P., cand tech sci; SHEVCHENKO, A. A., doctor of  
tech sci, and MELIKSETYAN, S. A., cand tech sci

[Abstract] Electrofilters used to entrap corrosive aerosols in nonferrous metallurgy, mineral fertilizer production and other industries, are made of nickel-containing stainless steel, lead, ferrosilide and other costly and scarce metals. Replacing these metals with polymers requires a study of their behavior under the effects of constant corona discharge and spark-over in the electrode gap and in the presence of a chemically corrosive medium (5-20% sulfuric acid, fluorine, sulfur, etc.). The stability of the polymers under these conditions has been shown to depend on the thermal and fire-resistance of the polymers, but the effects of thermal conductivity have not been studied. In the present work, a study was made of the effects of various carbon fillers on the thermal conductivity of polyethylene and polypropylene polymers. Acetylene carbon black is highly adsorptive and its particles become enveloped with the polymer material, while graphite is an inert filler in polypropylene. Because of similarity in structure, carbon black graphite filled polymer system provides high electro-thermal conductivity. Various variants of electrode materials have been worked out and resulted in a savings of 500,000 rubles. References 4: all Russian.  
[184-83440972]

ANALYTICAL CHEMISTRY

UDC 543.42:542.944

USE OF REACTION GAS EXTRACTION IN ATOMIC-EMISSION ANALYSIS WITH INDUCTIVELY COUPLED PLASMA

Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 39, No 2, Feb 84 (manuscript received 29 Mar 83) pp 215-220

KUZNETSOV, L. B., BELYAYEV, V. N. and BALUDA, V. P., State Scientific Research and Design Institute of Rare Metal Industry, Moscow; Moscow Institute of Steel and Alloys

[Abstract] Atomic emission spectrometer with inductively-coupled plasma was used in developing an analytical method for elements forming volatile chlorides (Si, Ge, B, As, P, Sn, Sb and Ti). Test samples were chlorinated with  $CCl_4$  in sealed quartz glass ampules. An apparatus was developed for introduction of gaseous chlorides into plasma. The accuracy of this method was verified by analysis of known quantities of Si and As. The analytical signal appeared to be independent of the composition of the test sample. The sensitivity of this method was  $4-5 \cdot 10^{-5}$  % for Si and  $1-2 \cdot 10^{-5}$  % for As, for 200-mg test samples. Improvements in the chlorination procedure could lead to further increase in the limits of detection. Figures 4; references 9: 2 Russian, 7 Western.

[202-7813]

UDC 543.422

REGULARITIES OF THERMAL DISSOCIATION PROCESS OF OXIDES IN GRAPHITE OVENS FOR ATOMIC ABSORPTION ANALYSIS

Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 39, No 2, Feb 84 (manuscript received 24 Mar 83) pp 221-231

L'VOV, B. V. and FERNANDES, G. Kh., A., Leningrad Polytechnic Institute imeni M. I. Kalinin

[Abstract] The goal of this work was to expand theoretical and experimental studies of the processes involved in oxide atomization. It was based on

newly developed methods of the determination of absolute process rates and characteristic behavior of oxygen in heated graphite ovens. Theoretical concepts of oxide thermodissociation were refined or developed de novo. Two typical thermodissociation patterns were identified: an isobaric mode controlled by external protective gas and an equimolar one regulated by the oxygen obtained from the decomposed oxide material. Thermodissociation of molecular oxygen exhibited a direct effect on the thermal chemistry of the process. For atomization of Be, Mg, Ca, Sr, Ba, Mn, Ga, In, Cr and V, energies of activation and the Arrhenius equation preexponential terms were determined. It was shown that in spite of the differences in construction and variability of material used in ovens, quantities of samples being evaporated, the rate of heating and different recording methods, all data could be interpreted on the basis of theoretical concepts of thermodissociation of oxides. Above results agreed well with data calculated using the diffusion model of vaporization. Figures 4; references 29: 14 Russian, 15 Western (3 by Russian authors).

[202-7813]

UDC 543.541.183.49

#### USE OF CARBOXYLIC ACIDS AS COMPLEX FORMING REAGENTS IN ION EXCHANGE CHROMATOGRAPHY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 39, No 2, Feb 84  
(manuscript received 4 Mar 83) pp 246-250

ZIMINA, I. F., IGNATOVICH, A. I. and KOROBACH, T. P., Belorussian State University imeni V. I. Lenin, Minsk

[Abstract] In an attempt to determine optimal conditions for the use of benzoic and hydroxybenzoic acid, EDTA and phthalein complex as eluants for chromatography of metal ions, the effect of pH and concentration of organic acid (or its salt) in the solution was investigated as it affected metal ions sorption by pretreated ion exchange resin AB-17x2. The strength of the complexes formed was the determining factor in binding metal ions to the exchange resin. A number of chromatographic separation profiles were reported. Separation factors were tabulated for transition and alkaline earth metals chromatographed under optimal conditions. Figures 3; references 11: 10 Russian (1 by Western author), 1 Western.

[202-7813]

UDC 543.53.064:546.621

NEUTRON ACTIVATION ANALYSIS OF HIGH PURITY ALUMINUM : RADIOCHEMICAL VARIETY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 39, No 2, Feb 84  
(manuscript received 28 Mar 83) pp 286-289

USMANOVA, M. M., KUZNETSOV, R. A., YANKOVSKAYA, T. A., KHOLYAVKO, Ye. P.  
and KHODZHAMBERDYEEVA, A. A., Institute of Nuclear Physics, UzSSR Academy  
of Sciences, Tashkent

[Abstract] Production of ultrapure aluminum requires that new quality control methods be developed. Analytical methods for residual impurities must be refined. The radiochemical methods described in literature are based, as a rule, on isolation of individual elements and therefore are cumbersome multistage processes. A simple radiochemical analysis of aluminum was developed based on neutron activation analysis. The method combines selective removal of matrix  $^{24}\text{Na}$  by adsorption on hydrated antimony(V) oxide from an irradiated sample solution in 10 M HCl with high resolution semiconductor gamma-spectrometry. Analytical characteristics of instrumental and radiochemical variants of neutron activation aluminum analysis were compared. The sensitivity of this method is in the range of  $5 \cdot 10^{-5}$  to  $2 \cdot 10^{-10}$  rel-% for up to 20 impurity elements. Figure 1; references 10: 2 Russian, 8 Western.  
[202-7813]

UDC 535.372:541.49:546.65

LUMINESCENCE OF YTTERBIUM COMPLEXED WITH 1-(2-PYRIDYLATO)-2-NAPHTHOL AND ITS  
USE IN ANALYSIS

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 39, No 2, Feb 84  
(manuscript received 20 Apr 83) pp 300-302

KOROVIN, Yu. V., MESHKOVA, S. B. and POLUEKTOV, N. S., Physical-Chemical  
Institute, UkrSSR Academy of Sciences, Odessa

[Abstract] It was of interest to investigate the luminescence ability of ytterbium complexed with organic compounds and to explore this in analysis. The organic complexing agent selected was 1-(2-pyridylato)-2-naphthol (PAN). Luminescence spectra were registered on a spectrometer SDL-1 using a mercury lamp DRSH-250. Luminescence spectra were registered in the range 960-990 nm, with a maximum at 980 nm. The luminescence was due to the transition  $^{1}\text{F}_{5/2} \rightarrow ^{2}\text{F}_{7/2}$ . The ratio of Rb:PAN in the complex was 1:2. Presence of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$  and  $\text{Lu}^{3+}$  did not interfere with the determination; other rare earth elements lowered the luminescence intensity. In the concentration range 0.1 to 10  $\mu\text{g}/\text{l}$  the luminescence intensity was linear. The sensitivity of this method is 0.05  $\mu\text{g}/\text{l}$ . Figures 2; references 9: 3 Russian, 6 Western (1 by Russian authors).  
[202-7813]

DETERMINATION OF MICROIMPURITIES OF IRIDIUM BY LASER ATOMIC FLUORESCENCE  
ANALYTICAL METHOD

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 39, No 2, Feb 84  
(manuscript received 1 Apr 83) pp 320-324

BOL'SHOV, M. A., ZYBIN, A. V., KOLONINA, L. N., MAYOROV, I. A., SMIRENKINA,  
I. I. and SHIRYAYEVA, O. A., Institute of Spectroscopy, USSR Academy of  
Sciences, Troitsk; State Scientific Research and Design Institute of Rare  
Metal Industry, Moscow

[Abstract] An attempt was made to develop a methodology for determining iridium--one of the most difficult elements to analyze--in industrial sulfate solutions by means of laser atomic fluorescence analysis. Under optimal conditions a linear calibration curve was obtained for iridium concentrations in the range of  $5 \cdot 10^{-3}$  to 100  $\mu\text{g}/\text{l}$ . Analytical results could be obtained in this fashion without isolation of iridium, because accompanying platinum metals did not interfere with the process. Comparison of the results with those obtained by atomic absorption technique which required preliminary isolation of iridium showed excellent agreement. Figure 1; references 8: 6 Russian, 2 Western (1 by Russian authors).

[202-7813]

BIOCHEMISTRY

UDC 543.253:547.7.462:577.15/17

ELECTROCHEMICAL BEHAVIOR OF BIOLOGICALLY ACTIVE DERIVATIVES OF BUTENEDIOIC ACID HETERYLAMIDES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 13 Jul 82) pp 410-414

SHAPOVALOV, V. A., KABACHNYY, V. I., SOPEL'NIK, E. M. and CHERNYKH, V. P., Kharkov State Pharmaceutical Institute

[Abstract] The mechanism of the cathode reaction of electron transfer with the participation of biologically active derivatives of butenedioic acid heterylamides in which two carbonyl groups of the side chain are conjugated through an ethylene bridge was studied. The electrochemical reduction mechanism of butenedioic acid 5-R-2-(1,3,4-thiadiazolyl)amides includes constant transfer of two electrons at the acylamide fragment on the side chain. The antihypoxic activity of the substances was found to be in symbiotic relationship with the ease of reduction. Figures 2; references 9 (Russian).

[196-83440972]

UDC 577.156:547.1'118

SPECIFICITY OF SUBTILISIN CARLSBERG IN REACTION WITH O-n-ALKYL-p-NITROPHENYL METHYLPHOSPHONATES

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 33, No 1, Jan-Feb-Mar 84 (manuscript received 21 Sep 83) pp 62-63

AAVIKSAAR, A., PEYPS, M. and SIKK, P., Institute of Chemical and Biological Physics, Estonian SSR Academy of Sciences

[Abstract] In a publication by this laboratory together with the Laboratory of Protein Chemistry, All-Union Scientific-Research Institute of Genetics and Selection of Industrial Microorganisms, Glavmikrobioprom, the feasibility of using organophosphorus inhibitors of serine esterases to study the topography of the active sites of bacterial proteinases was demonstrated.

Since then, it has been shown that subtilisens BPN', and Carlsberg, are not exoproteinases for two strains of one *Bacillus subtilis* species, but are synthesized by a different species of bacillus. The producer of subtilisens BPN' was *Bacillus amyloliquefaciens*, and that of subtilisens Carlsberg was *Bacillus licheniformis*. To clarify whether or not any difference appears in the primary structures of subtilisens BPN' and Carlsberg in specificity in the reaction of low molecular substrates and inhibitors, a study was made of the kinetics of irreversible inhibition of subtilisens Carlsberg in the reaction with O-n-alkyl-p-nitrophenyl methylphosphonates. A comparison of bimolecular rate constants shows that increasing the number of carbon atoms in the normal alkoxy radical of the phosphoryl part of the inhibitor from 2 to 6 results in a 10-fold increase in the rate constant for phosphorylation of the active site of the enzyme. Figures 1; references 6: 1 Russian, 5 Western.

[185-83440972]

CATALYSIS

UDC 547.216:542.941.8:66.095.252.7:542.973:546.73

EFFECT OF COBALT ADDITIVES ON PHYSICAL CHEMICAL AND CATALYTIC PROPERTIES OF ALUMINUM PLATINUM CATALYSTS IN REACTIONS OF DEHYDROCYCLIZATION AND DEHYDROGENATION OF n-HEXANE

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received 25 Dec 81) pp 22-27

NADIROV, N. K., LYKOVA, L. F., PETROSYAN, L. S. and VOZDVIZHENSKIY, V. F., Institute of Chemistry of Petroleum and Natural Salts, Kazakh SSR Academy of Sciences, Guryev

[Abstract] Although cobalt and its compounds are widely used as catalysts in hydrocarbon synthesis, oxosynthesis, isomerization, polymerization, etc., little work has been done on the use of cobalt to synthesize catalysts for hydrocarbon aromatization. In the present work, cobalt was used to prepare aromatization catalysts. Its effects of dehydrocyclization and dehydrogenation reactions and the physical mechanical properties of cobalt modified aluminum platinum catalysts were studied. Platinum aluminum catalysts modified with 0.5-1:1 cobalt:platinum increase the benzene yield from n-hexane in dehydrocyclization reactions, while aromatization of n-hexane was found to pass through an intermediate stage of hexene and methylcyclopentane formation. Introduction of cobalt also raises the mechanical stability of aluminum platinum catalysts and decreases the platinum particle size.

Figures 4; references 9: 8 Russian, 1 Western.

[198-83440972]

UDC 665.659.72

SYNTHESIS OF HYDROCARBONS FROM CO AND H<sub>2</sub> OVER Co-ALUMINOCALCIUM CATALYSTS,  
MODIFIED WITH CUPRIC OXIDE

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received  
25 Mar 83) pp 45-48

LAPIDUS, A. L., BRUK, I. A., SOMINSKIY, S. D., FRANKFURT, G. I., GOLOSMAN,  
Ye. Z., NECHUGOVSKIY, A. I. and YAKERSON, V. I., Institute of Organic  
Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences; Novomoskovskiy  
Branch, State Scientific Research and Design Institute of the Nitrogen  
Industry and of Products of Organic Synthesis

[Abstract] The search for new and effective catalysts for hydrocarbon  
synthesis from carbon monoxide and hydrogen is becoming more pressing as an  
alternate solution to the fuel and energy problem. Cobalt-aluminum-calcium  
catalysts are promising although they must first be reduced at temperatures  
exceeding 500°C. In the present work it was shown that when these catalysts  
are modified with cupric oxide, the reduction temperature may be lowered by  
100-150°C and the yield of liquid C<sub>4</sub>-C<sub>10</sub> hydrocarbons increased by 18-25%  
while the yields of methane and carbon dioxide are also increased. Figures 2;  
references 8: 5 Russian, 3 Western.

[198-83440972]

UDC 547.313.3:542.941.7:66.094.173:546.719

PROPERTIES OF RHENIUM-COATED CATALYSTS IN HYDROGENATION OF PRODUCTS OF  
HYDROFORMYLIZATION OF PROPYLENE

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received  
31 Dec 82) pp 49-52

RYASHENTSEVA, M. A., MINACHEV, Kh. M. and ANIKEYEV, I. K., Institute of  
Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences

[Abstract] It was shown previously that rhenium catalysts are capable of  
reducing the carbonyl group into hydroxyl at high temperature and hydrogen  
pressure. In the present work a study was made of rhenium and bimetallic  
rhenium/copper and rhenium/nickel on gamma-alumina hydrogen sulfide treated  
catalysts in the conversion of propylene containing 40% butyric aldehyde.  
Butyric aldehyde was converted to butyl alcohol at 99-100% and 95% yields,  
respectively, over hydrogen sulfide treated catalysts consisting of 7%  
rhenium on alumina and 5% nickel and 1% rhenium on alumina at 160-180°C,  
30 MPa pressure and 4-5 hours<sup>-1</sup> space velocity. References 10: 6 Russian,  
4 Western.

[198-83440972]

UDC 547.245

NEW HETEROGENEOUS METAL COMPLEX CATALYSTS FOR HYDROSILYLATION REACTIONS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 23 Mar 83) pp 354-356

POMERANTSEVA, M. G., BELYAKOVA, Z. V., SHCHEPINOV, S. A., YEFIMOVA, L. A. and CHERNYSHEV, Ye. A., State Scientific Research Institute of Chemistry and Technology of Heteroorganic Compounds, Moscow

[Abstract] One of the most important trends in the development of hydrosilylation reactions is the search for new catalysts, such as metal complexes in which the metal atom is coordinately bound to a polymeric carrier acting as a macroligand. In the present work platinum and rhodium complexes with polyconjugated polymers were heat-treated to form new metal complexes having multiply bound polyconjugated chains of metal atoms. These catalysts were found to exhibit high activity in hydrosilylation reactions. References 7: 4 Russian, 3 Western.

[196-83440972]

UDC 541.49:541.128:546.98:547.556

COMPLEXES OF PALLADIUM (II) WITH CERTAIN AZO COMPOUNDS AND THEIR CATALYTIC PROPERTIES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 9 Dec 82) pp 385-388

SAFRONOVA, L. A., SHEBALDOVA, A. D. and KHIDEKEL, M. L., Scientific Research Institute of Chemistry of the Saratov State University imeni N. G. Chernyshevskiy

[Abstract] Platinum (II) complexes with ortho-substituted azo compounds were prepared in a previous work and their catalytic activity and selectivity in nitrobenzene hydrogenation reactions were demonstrated. In the present work, palladium (II) complexes were formed with 4-(2-piperidylazo) resorcinol, 1-(2-piperidylazo)-2-naphthol, and 1-(2-naphtholazo)-4-sulfonylbenzene. These complexes were found to have high catalytic activity and stability under mild conditions in nitrobenzene hydrogenation reactions.

Figures 2; references 7: 6 Russian, 1 Western.

[196-83440972]

CHEMICAL INDUSTRY

CHEMICAL PRODUCTION INCREASING

Moscow SEL'SKAYA ZHIZN' in Russian 1 Feb 84 p 1

[Unsigned article: "A Giant of Chemistry Is Growing"]

[Text] Kalush (Ivano-Frankovsk Oblast)--The work collective of the Kalush Association "Khlorvinil" [Chlorvinyl] has significantly increased deliveries of caustic soda to chemical industrial enterprises. Here, the first line of a production complex, expected to produce an annual output of 125,000 tons of raw material for obtaining chemical fibers, cleansing agents and other synthetic materials, has been put into operation.

The Chlorvinyl Association, which already makes more than 40 types of products, is continuing to grow. Here, construction of a large factory for the production of ethylene has begun.

12596

CSO: 1841/189

## COAL GASIFICATION

UDC 66.074.7/66.074.378.1

### REMOVAL OF HYDROGEN SULFIDE IN INDUSTRIALLY REFINED SHALE GENERATOR GAS TO OBTAIN FINISHED PRODUCTS

Moscow KHMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 2, Feb 84 p 16

AFANASIYEV, Yu. M., GOLYAND, S. M., BELYUGA, Yu. V. and RYBAKOV, L. A.

[Abstract] When fuel gases resulting from shale gasification have a low hydrogen sulfide to carbon dioxide ratio, they are purified by a selective oxidation process such as the modified arsenic-soda method with catalytic regeneration of the absorber solution. In Kokhtla-Yarve (Estonia) this method is further modified so that the saturated absorber solution is regenerated with 3 mg/liter of cobalt sulfophthalocyanine in a hollow horizontal absorber. Generator gas from five stations and the "Kiviter" installation, amounting to 175,000 m<sup>3</sup>/hr, is treated. Pure sulfur is recovered as a foamy pulp. Pentahydrate crystals of thiosulfate are recovered from the sulfur foam filtrate. The purified gases containing up to 600 ppm hydrogen sulfide are used as heating fuel. Purification of generator gas from hydrogen sulfide results in a 10-fold decrease in release of sulfur dioxide into the atmosphere. Figures 1; references 1: Russian.

[184-83440972]

UDC 662.749.41

### PHENOL COMPOSITION OF HEAVY SHALE OIL RESINS

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 33, No 1, Jan-Feb-Mar 84 (manuscript received 18 Feb 83) pp 1-8

NAPPA, L., KLEMENT, I. and VINK, N., Institute of Chemistry, Estonian SSR Academy of Sciences

[Abstract] A study was made of the phenol composition of heavy shale oil resins obtained by catalytic hydrogenation and by low temperature conversion.

The substances studied were a mixture of alkyresorcins separated by partial dephenolization from bottom distillate, and the total phenols obtained by semicoking of Kukersite shale. Despite the low temperature (370°C), the degree of decomposition by conversion, especially in the water phase, was much higher than by catalytic hydrogenation. Alkylresorcinols in both cases are very unstable and only a small quantity of monohydric low boiling phenols are formed. Product analysis shows that conversion and hydrogenation proceed by different mechanisms. The results of the study indicate that the phenol composition has to be studied further by deep fractionation of total phenols and selective determination or elimination of functional groups.

Figures 6; references 5: 3 Russian, 2 Western.

[185-83440972]

UDC 620.193.94

#### CATALYSIS AND INHIBITION OF THERMAL DESTRUCTION OF HYDROCARBONS

Tallinn IZVESTIYA AKADEMII NAUK ESTONSKOY SSR: KHIMIYA in Russian Vol 33, No 1, Jan-Feb-Mar 84 (manuscript received 27 Apr 83) pp 39-44

AARNA, A., VASIL'YEV, V. AND ZHIRYAKOV, Yu., Institute of Chemistry, Estonian SSR Academy of Sciences; Scientific Research Institute of Shales, Production Association "Slantsekhim" imeni V. I. Lenin

[Abstract] The gasoline produced during semicoking of shale oil is an active corrosion inhibitor during pyrolysis of hydrocarbon feed stock, but it does not suppress coke formation. Its influence on the thermal destruction of hydrocarbons is mainly due to lowering the concentration of unsaturated protons in the pyrolysate. Using this gasoline as a corrosion inhibitor under production conditions will inhibit formation of pyrocarbon. The presence of nickel in the pyrolysis equipment results in benzene losses and high coke formation in the production of aromatic hydrocarbons. Nickel also causes destruction of unsaturated feed stock components. Ferric oxide actively catalyses the formation of unsaturated compounds and coke. A possible mechanism is proposed for coke formation during benzene pyrolysis in the presence of nickel. Figures 3; references 5: 4 Russian, 1 Western.

[185-83440972]

COMBUSTION

UDC 541.126+542.943

PATTERNS OF ACCUMULATION OF REACTION PRODUCTS IN STABILIZED COOL PROPANE FLAME

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian No 1, Jan 84 (manuscript received 30 Nov 82) pp 53-55

POGOSYAN, M. DzH., GUKASYAN, P. S., POLADYAN, Ye. A. and MANTASHYAN, A. A., Institute of Chemical Physics, Armenian SSR Academy of Sciences, Yerevan

[Abstract] Concentration profiles of reaction products along the vertical cross section and along the length of the reactor in the zone of a stabilized cool propane flame at various rates of flow and various temperatures are analyzed and described. It was found that concentrations of all reaction products increase along the horizontal axis of the reactor, reach a certain magnitude and then remain virtually unchanged. The rate of gas flow and not the temperature has the greatest effect on the concentration profile. The cool flame may be extended along the entire reactor cell or is retained at the reactor beginning. Figures 4; references 9: 8 Russian, 1 Western.  
[216-2791]

## FERTILIZERS

### FERTILIZER LOSSES AND CHAOTIC DELIVERY

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 17 Mar 84 p 1

[Article by V. Yapparov, apparatchik of the Carbamid Factory, member of the CPSU Salavatskiy Municipal Committee; B. Maksimov, chairman of the group of Peoples Control of the "Salavatnefteorgsintez" Association; T. Nekrasova, acting head of the Transportation Services Section of the Moldavian Railroad; E. Skalatskiy, inspector of the Moldavian SSR; S. Savrukov, head of the section of the Kazakh SSR; E. Leont'eva, reviewer for SOTSIALISTICHESKAYA INDUSTRIYA: "Unjustifiable Losses: Tracing the Journey of Mineral Fertilizers from Supplier to User"]

[Text] Last year collectives of enterprises that produced mineral fertilizer did a fine job. On the whole, the plan of deliveries was overfulfilled by 250,000 tons, partially making up for the first years of the Plan. In this, merit belongs to the railway workers who helped to transport the over-filled warehouses of a number of enterprises. In the first months of the New Year, however, the situation with the shipment of fertilizer became complicated. Collective farms and state farms received less than the planned amount of phosphorus, as well as nitrogen fertilizer. And this occurred at a time when the laborers of a village actively prepare for spring planting. The travelling brigade of "Socialist industry" decided to ferret out the reasons for such a situation.

At the carbamide factory of the "Salavatnefteorgsintez" Association tens of thousands of tons of fertilizer are preserved in a very large warehouse, like a gravel mine. The carbamide runs in a steady stream from the transporter and a bulldozer spreads the white snowdrifts to all the corners. In places the drifts have reached to the roof itself. The fertilizer will not be removed for some time, it will spoil in storage and then much effort will be required to break up the lumps that have formed. In this way much carbamide is pulverized and loses its quality.

In an adjacent warehouse, piles of bags have grown up to 8 meters. Workers have their smoking break here. Here are notices in a journal: they stood in expectation of an empty car for 6 hours, 8, 11.... In January the Bashkir section of the Kuybyshev Railway failed to deliver 107 railway cars to the factory, in February the same number for half a month. To the same factory the railway workers had to return 800 powder cars for the month-- there was no way to repair them.

The factory overproduced their January plan of 4,200 tons of products and exceeded the February plan as well. By doing this the net cost of fertilizers was lowered by 1/2 a percent. "Vitamins" for the fields go along the transporters in a thick flow and...sit in warehouses.

It is true that A. Vishnevskiy, head of that section of the railway, did visit the Association. Things were somewhat corrected, but 32,000 tons still remained.

The situation, taking shape for the Bashkir chemists, it must be said, is not an exception to the rule. Such enterprises as the Balakovskiy and Rossoshanskiy 60th Anniversary of the USSR chemical factories, the Dorogobuzhskiy factory of nitrogen fertilizers, "Tol'yattiazot," and a number of associations that produce phosphorus fertilizers do not fulfill their delivery plans. You'll not dismiss the shortcomings of these collectives with calculations. But more often than not the reason for the backup is the arhythmic delivery of empty cars. For 20 days of February the MPS [Machine Repair Station?] failed to deliver to the chemists approximately 300,000 cars.

To carry out that which has been stored in warehouses of enterprises on the eve of the spring sowing is the most important task of transportation workers. But here, it turns out, several points of the Railway Regulations may hinder this. Let's take as an example the Dzhambul superphosphate factory which recently was considered outstanding. This year its collective became one of the initiators of a competition of workers collectives of Kazakhstan. Another large enterprise of the Republic, the Khimprom Association began to work more diligently. Chemists increased the output of manure and mineral additives for fodder. Along with this, both enterprises last year could not ship out to "small" users tens of tons of fodder phosphates. Shipments are being held back even now. What's going on here?

"We cannot carry less than 60 tons on a railway car," the railway workers throw up their hands. Does it turn out that the situation is irresolvable? From the point of view of those who are inclined to hide behind the regulation, the problem is unsolvable. But if only the leaders of those enterprises, A. Yegorov and M. Atabayev--together with the leader of the Alma-Ata Railway, K. Kopzhasarov, would depart from the usual rule citation, then a solution would be found. True, there exists the so-called small shipments in the guise of baggage or containers. Troublesome? Yes, of course. But it is impossible to wave off small deliveries on this basis.

Fertilizers lying in warehouses are already part of lost production. Here the losses are valuable time and losses of quality and losses of human labor. But this is not all. As the USSR Ministry of Agriculture reported recently, shipments of fertilizers in unprepared transports have increased and thus fertilizers are lost along the railway. At their destination significantly less arrives than is shown on their accompanying documents.

Let's go to the user to make sense of this.

The situation is tense at the facilities of the Slobodzeiskiy Interrayon Association "Moldselkhozhimiya": the unloading of cars that have arrived from the Cherkass Association "Azot" is underway. A rapid unloader, similar to a small tractor, is hopelessly clogged. I. Kananeu, the operator, digs near it, uncoiling from a husk scraps of cloth and picks out slivers from the mechanism.

These are the kind of "little gifts" that we receive from Cherkass, from the Pridneprovskiy chemical factory, the Odessa superphosphate--he relates indignantly. The floor has gotten worse, they spread rags, paper, put down boards. But this does not save it from loss. It is readily apparent that manure has "fertilized" the railway line. And how many times does the unloader simply let it fall through the bottom that is full of holes!

It turns out that there is something to ask not only from those who prepare the fertilizer for transport and who ship it, but also from those who accept it. Granules of productivity often fall next to the embankment and are kept under the open sky. "Moldsel'khozhimiya" is only half supplied from warehouses, and unsuccessfully deals with access roads.

In other regions the situation is even more tense. "Ukresel'khozhimiya" for example, is supplied by rail warehouses for chemical production only up to 33 percent. In oblasts such as Astrakhán, Omsk, Amur, this figure is even lower, 25-30 percent. But the Saratov regional agricultural chemistry enterprise (chairman V. Dukhovnov) is worst of all in worrying about the receipt of fertilizer. There, the supply by warehouses is only 20 percent of that needed. As a result, at many stations of the oblast mineral fertilizers must literally be delivered by falling down a slope.

When they deliver the product in an unsuitable wagon, filled with holes, one can only get it off your hands and give a reprimand. This is not only a material loss, but it is an enormous spiritual loss, taking place without punishment before the eyes of many persons. It is possible to assess the facts when those, for whom the fertilizer is intended, forget that they are dealing with the economy.

We have arrived at one of the largest southern station bases in Strashen. On entering the warehouse it was not necessary to ask what was stored here: a red liquid underfoot unmistakably pointed to potassium chloride. In a pit water glistened; they will never kick the fertilizer here into the soil. A group of workers is shoveling granules from one pile to another, creating an arbitrary composition from superphosphate and potassium chloride. In the warehouse where the hoppers are unloading, fertilizers are willy-nilly mixed with snow which they have neglected to clean up...

Several steps from the office of the base two railway cars have become frozen with ammonium nitrate. When we approached, one of them had been standing there for 3 hours, the other for more than 7. From this it is understandable why railway cars standing here have twice exceeded the norm.

We asked the substitute chairman of the local association of agricultural chemistry Yu. Izman to explain why order is absent at the base.

Yu. Izman throws up his hands. What do you want, he says, we cannot succeed because it is necessary to unload manually.

The argument is clearly not in favor of the responsible person. So the unloaders draw the fertilizer on their shoulders. It could work otherwise. In the port of Odessa, for example, they introduced the aggregate by processing the loads in sacks--2,000 sacks per hour. It means that the engineers are thinking, searching. It is possible to lower the expenditure of labor by using wooden trays.

So, maybe it is necessary not to complain but to go directly to a constructive thought. Don't complain about the garbage, as they say, but take the broom and sweep it. In any case the observing of elementary rules of preserving fertilizer for the collective's base is not fully under control.

The number of idle railway cars during unloading is great at many bases, which complicates the work of the railway transport even more. Here are several figures. Last month at the Pallasovka Privilzhskaya Railway Station the rayon Agricultural Chemistry Association unloaded railway cars for 45 hours instead of 9. In Millerov of the Yugo-Vostochnaya Railway they hurried even more slowly: instead of 2.3 hours the railway cars stood 44 hours while being unloaded. In the Association Mirnensk of Agricultural Chemistry the above-norm period of idleness was 42 hours per railway car. Is it possible to speak of organization and order here?

12596  
CSO: 1841/189

CHEMICAL PLANT ON STREAM

Moscow SEL 'SKAYA ZHIZN' in Russian 29 Feb 84 p 2

[Unsigned article: "Constructed"]

[Text] Novgorod 28 (TASS) Construction has been completed of a nitroammonium complex in the Novgorod Production Association "Azot."

The CPSU Central Committee heartily congratulated all the participants of the construction and activation of the production capacities of mineral fertilizers on their great labor victory.

Today in the municipal Palace of Culture and Technology a celebratory meeting was held at which N. A. Antonov, the first secretary of the Novgorod Oblast Committee of the CPSU, gave a welcoming address.

Those making presentations at the meeting assured the Lenin CPSU Central Committee and its Politburo that worker collectives of construction, fitters and operators, struggling for transforming into life the resolutions of the December (1983) and February (1984) Plenums of the Central Committee of the Party, will henceforth raise the effectiveness of production in all ways.

12596

CSO: 1841/189

UDC 631.83.84.85.893

NEW FERTILIZERS FOR CENTRAL ASIAN REPUBLICS

Tashkent UZBEKSKIY KHMICHESKIY ZHURNAL in Russian No 1, Mar 84 (manuscript received received 16 Feb 83) pp 38-41

KARMYSHOV, V. F., Scientific Research Institute of Fertilizers and Insecto-fungicides

[Abstract] A review is presented of current research on the development and application of fertilizers to serve the needs of agriculture in the Central Asian republics. Primary emphasis is presently placed on complex liquid fertilizers, with a discussion of the problems that attend their usage, such as environmental pollution due to soil erosion, leaching and volatization. Of particular interest in this regard are current efforts at the creation of capsulated forms of fertilizers and of granulated slow-release forms. The 20-20-0 liquid fertilizer can serve as an example of the application of new technology; this fertilizer is obtained by ammonization of polyphosphoric and nitric acids, and on gray desert soils has been shown to increase cotton harvests by 9 percent. References 17 (Russian).

[218-12172]

ORGANOMETALLIC COMPOUNDS

UDC 546.982+547.449+543.253

COMPLEX COMPOUNDS OF PALLADIUM (IV) WITH ARYLPHOSPHINES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 11 May 83) pp 282-288

BUSYGINA, T. Ye., POLOVNYAK, V. K. and AKHMETOV, N. S., Kazan Chemical Engineering Institute imeni S. M. Kirov

[Abstract] Complexes of palladium IV have not been studied in any depth. Phosphine ligands are known to stabilize both high and low states of oxidation in metals. In the present work the possibility of stabilizing the higher (+4) oxidation state of palladium with substituted arylphosphines was investigated. Complexes of  $PdL_2Cl_4$  (where L = arylphosphines) and dimeric acetate complexes of palladium were synthesized. The effect of the nature of the organophosphorus ligand on the electrochemical reduction of palladium IV complexes was studied. Thermal decomposition of palladium IV complexes was shown to undergo disproportionation into palladium III compounds. Figures 2; references 13: 11 Russian, 2 Western.

[196-83440972]

UDC 547.258.11+547.259.8

SYNTHESIS OF ARYLTRIMETHYLTANNANES BY REACTION OF  $Me_3SnSnMe_3$  WITH  $ArI$  CATALYZED BY 'LIGANDLESS' PALLADIUM

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 5, Feb 84 (manuscript received 8 Jun 83) pp 1103-1106

BUMAGIN, N. A., BUMAGINA, I. G. and BELETSKAYA, I. P., corresponding member, USSR Academy of Sciences, Moscow State University imeni M. V. Lomonosov

[Abstract] Recently the authors described the reaction of  $Me_3Sn_2$  with  $ArI$  catalyzed by  $(\pi-C_6H_5PdCl)_2$  in methylene chloride to synthesize aryltrimethylstannane with active functional groups (ZHURNAL ORGANICHESKOY KHMII Vol 17, 1981, p 905). Since much of the palladium catalyst was eliminated, the present article reports on further research into the role

of the solvent in reaction yield, using as solvents methylene chloride, acetonitrile, acetone, tetrahydrofuran(THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylphosphorotriamide (HMFTA). The reaction with 2,4-dinitroiodobenzene was conducted at  $25 \pm 0.1^\circ\text{C}$  with reagent concentration at  $5 \cdot 10^{-2}$  mol/l, and conversion and yields were measured using thin layer chromatography. Reactions in HMFTA and THF took place within about 10 minutes, while they were much slower in acetonitrile and methylene chloride. Unexpectedly, the slowest reaction of all took place in DMSO. Thus, the solvents had a major impact on reaction time and yields of  $\text{RSnMe}_3$  in dependence on their donor capacity, since they served on the one hand as ligands and, on the other hand, increased the reactivity of hexamethyldistannane. Results showed the optimum ratios to be in DMF and acetone. References 6: 3 Russian, 3 Western.

[187-12131]

## ORGANOPHOSPHORUS COMPOUNDS

UDC 547.26'118

### NEW TYPE OF FURANOSE BICYCLOPHOSPHITES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 4 Jan 83) pp 279-282

KOROTEYEV, M. P., LUTSENKO, A. I. and NIFANT'YEV, E. Ye.

[Abstract] A representative of a new type of sugar bicyclophosphite was synthesized for the first time. By reaction of a furanose containing free hydroxyl groups at the C<sup>2</sup>, C<sup>3</sup>, and C<sup>5</sup> positions, bicyclophosphites were obtained in which the phospholane ring condensed with the furanose ring of the sugar skeleton. Nuclear magnetic resonance spectra and chemical analysis of the compounds differ from those of 3,5,6-bicyclophosphites of furanose. The 2,3,5-bicyclophosphite of  $\alpha$ -methylmannofuranoside spontaneously isomerizes into the corresponding 3,5,6-bicyclophosphite. This is the first example of phosphite rearrangement. References 8: 5 Russian, 3 Western. [196-83440972]

UDC 547.33+547.34+547.78

### PREPARATION AND PROPERTIES OF 2-CHLORO-1-ACYLAMINOVINYLTRIPHENYLPHOSPHONIC ACID CHLORIDES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 25 May 83) pp 288-301

BROVARETS, V. S., LOBANOV, O. P., VINOGRADOVA, T. K. and DRACH, B. S., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] It was recently discovered that N-1,2,2-trichloroethylamides of acids react readily with triethylphosphite and triphenylphosphine, but the resulting phosphorylation products could not be studied because the required N-substituted amides of the type Cl<sub>2</sub>CHCHClN-acyl were difficult to prepare. In the present work, a new and simple method for preparing N-1,2,2-trichloroethylamides of aromatic acids by condensation of chloral with benzamide and its analogs was developed. Heating N-1,2,2-trichloroethylamides

of aromatic acids with triphenylphosphine resulted in 2-chloro-1-acylaminovinyltriphenylphosphonic acid chlorides, which are polyfunctional reagents suitable for the synthesis of new types of substituted vinyl-phosphonic salts, phosphorus-containing betaines and phosphorylated azoles. Figures 1; references 8: 7 Russian, 1 Western.  
[196-83440972]

UDC 547.26'118

#### ACYLATION OF DIALKYLPHOSPHITES WITH TRIFLUOROACETIC ANHYDRIDE: TRIFLUOROACYLPHOSPHITES AND TRIFLUOROKETOPHOSPHONATES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 2 Aug 82) pp 308-312

OFITSEROV, Ye. N., MIRONOV, V. F., KONOVALOVA, I. V. and PUDOVIK, A. N., Kazan State University imeni V. I. Ulyanov-Lenin

[Abstract] It was previously shown that trifluoroacylphosphites and trifluoroketophosphonates are intermediates in reactions of  $\alpha$ -phosphorylated trialkyl-, tetraalkylpyro- and dialkylacylphosphites with trifluoroacetic acid. It was assumed that trifluoroacetic anhydride was formed and that the latter, being a powerful acylating agent, must react further. To model these reactions and explain the formation of products in another work, dialkylphosphites were acylated with trifluoroacetic anhydride to form, depending on the reaction conditions and the reagent ratios, either diphosphonates or phosphorylated phosphates. These products result from reactions of the intermediate trifluoroketophosphonates. When the acylation was conducted in the presence of a base, diethyltrifluoroketophosphonate was formed at low yield. Figures 2; references 14: 5 Russian, 9 Western.  
[196-83440972]

UDC 547.546+547.241

#### N-NITROARYL-SUBSTITUTED PHOSPHAZIDES AND PHOSPHAZO COMPOUNDS, PART 1: ACID DECOMPOSITION OF PHOSPHAZIDES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 4 Feb 83) pp 325-333

ONYS'KO, P. P., PROKLINA, N. V., PROKOPENKO, V. P. and GOLOLOBOV, Yu. G., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] The phosphazides known to be stable are the intermediate products of a Staudinger reaction. A study was made of the influence of electronic and steric effects on the stability of phosphazides and some of their chemical properties. Stable phosphazides were prepared by reaction of

triphenylphosphine with nitroarylazides. The stability of the phosphazides was found to increase with the increasing electron-acceptor capability of the N-aryl group and also when spatial ortho-substituents are present in the N-aryl group. Acids or bases cause destabilization of N-nitroarylphosphazides. N-arylphosphazides decompose in the presence of acids to form arylamides and triphenylphosphine oxide. It was demonstrated that this decomposition does not pass through an intermediate phosphazo stage. Figures 1; references 15: 3 Russian, 12 Western.

[196-83440972]

UDC 547.241+547.412.92+547.525

ARYLBIS(HEPTAFLUOROPROPYL)PHOSPHINE OXIDES: ELECTRONIC NATURE OF P(O)  
(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 24 Dec 82) pp 334-339

YAGUPOL'SKIY, L. M., PAVLENKO, N. V., IGNAT'YEV, N. V., MATYUSHECHEVA, G. I. and SEMENIY, V. Ya., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Since perfluoroalkyl radicals are similar to each other in electronic nature, the  $\delta$ -constants of the (RF)<sub>2</sub>P(O) group were determined, and for this purpose phenyl- meta- and para-fluorophenylbis(heptafluoropropyl)phosphine oxides were synthesized by hydrolysis of the corresponding arylbis(heptafluoropropyl)dichlorophosphoranes. The phenyl esters and anilides were prepared by reaction of bis(heptafluoropropyl)phosphonic acid chloride with substituted phenols and anilines. The  $\delta$ -constants of the P(O)(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>, OP(O)(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub> and NHP(O)(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub> groups were then determined by nuclear magnetic resonance. The P(O)(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub> group is very close in electronic nature to the -SO<sub>2</sub>CF<sub>3</sub> group, one of the strongest electron-acceptor groups. Figures 1; references 12: 4 Russian, 8 Western.

[196-83440972]

UDC 547.26'.118.07

CHEMICAL CONVERSIONS OF PHOSPHORUS ACID HYDRAZIDES, PART 3: REACTION OF PHOSPHORUS ACID HYDRAZIDES WITH STEROIDS AND SOME PHYSICAL-CHEMICAL PROPERTIES OF REACTION PRODUCTS

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 25 Oct 82) pp 436-440

OVRUTSKIY, V. M., PROTSENKO, L. D., VOLOVEL'SKIY, L. N., POPOVA, N. V., BOLDESKUL, A. Ye., VINNIKOVA, A. V. and CHERNOVA, T. M., Kiev Scientific Research Institute of Pharmacology and Toxicology; Kharkov Scientific Research Institute of Endocrinology and Chemistry of Hormones

[Abstract] In view of the increase in physiological activity when the C=O group in position 3 of the A ring is replaced with a C=N group, a study was made of the synthesis conditions of O-aryl-N,N-di(2-chlorethyl)hydrazone of dihydrotestosterone and its benzoate. These compounds were prepared by reaction of phosphorus acid hydrazides containing a chloroethylamino group with steroids (dihydrotestosterone and its benzoate). The ionization constants of the above were determined and the effects of substituents of various electronic nature on the basicity of the phosphorus acid hydrazone was demonstrated. The basicity of the phosphorus acid hydrazone was found to be related to its structure, and the imine nitrogen atom in the hydrazone group was shown to be more basic. Figures 1; references 12: 8 Russian, 4 Western.

[196-83440972]

UDC 547.341

PHOTOINITIATED ADDITION OF PHOSPHORUS TRIBROMIDE TO ALKOXYETHENES

Leningrad ZHURNAL OБSHCHEY KHIMII in Russian Vol 54, No 2, Feb 84 (manuscript received 12 Apr 83) pp 457-458

SHILOV, S. A., SENDYUREV, M. V., DOGADINA, A. V., IONIN, B. I. and PETROV, A. A., Leningrad Technologic Institute imeni Lensoveta

[Abstract] According to another work, phosphorus trihalides react by addition to alkoxyalkyl to form alkenephosphones in which the dibromophosphine group is in a vicinal position with respect to the alkoxy group. In the present work, it is demonstrated that the photoinitiated reaction of phosphorus tribromide with alkoxyethenes results basically in the E-isomer of the adduct in which the dibromophosphine group is in a geminal position in respect to the alkoxy group, as confirmed by paramagnetic resonance spectra. References 3 (Russian).

[196-83440972]

UDC 547.26'118+547.421.51'26

REACTION OF ACETALS CONTAINING CARBONYL GROUP AT ALCOHOL FRAGMENT WITH PYROCATECHINCHLOROPHOSPHITE IN PRESENCE OF TRIALKYLPHOSPHITES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 9 Mar 83) p 459

GAZIZOV, M. B., SHERGINA, I. I., KHAYRULLIN, R. A., SHCHELKUNOVA, M. A., OSTANINA, L. P. AND KRASII'NIKOVA, Ye. A., Kazan Chemical Engineering Institute imeni S. M. Kirov

[Abstract] Pyrocatechinchlorophosphite, in the presence of trialkylphosphites, reacts with acetals containing a carbonyl group at the alcohol fragment with two phosphorus atoms of differing coordination. The physical constants and alkyl groups for the compounds are listed.

[196-83440972]

UDC 547.26'118

REACTIONS OF DIMETHYLISOCYANATOPHOSPHITE WITH DIISOPROPYLTRIFLUOROACETYLPHOSPHONATE

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 11 Jul 83) p 463

KONOVALOVA, I. V., KASHTANOVA, N. M., BURNAYEVA, L. A. and PUDOVIK, A. N., Kazan State University imeni V. I. Ulyanov-Lenin

[Abstract] Dialkylisocyanatophosphites were previously shown to form cyclo-addition products with  $\alpha$ -ketophosphonates. In the present work, diisopropyltrifluoroacetylphosphonate was shown to react exothermally with dimethylisocyanatophosphite. By conducting the reaction carefully under anhydrous ether and with cooling, a crystalline compound was formed which corresponds to 5-diisopropoxyphosphonyl-2,2-dimethoxy-5-trifluoro-methyl-4-oxo-1,3,2-oxazophosphol-3-ene. In contrast to azaphospholenes, this compound does not undergo imide-amide rearrangement. References 2 (Russian).  
[196-83440972]

UDC 547.1'118

NEW DIRECTIONS IN REACTIONS OF SILYLPHOSPHITES WITH ACETYL CHLORIDE

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 4 Jul 83) pp 464-465

AL'FONOSOV, V. A., ZAMALETINOVA, G. U., BATYYEVA, E. S. and PUDOVIK, A. N., Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Dialkylsilylphosphites react with acylhalogenides via the Arbuzov reaction to form acylphosphonates. The authors also found that diethyltrimethylsilylphosphite reacts with acetyl chloride in the presence of triethylamine to form bis(diethylphosphono)trimethylsilyloxymethane and diethylphosphono-1-trimethylsiloxyethylene. Apparently, silylphosphites can react with acetyl chloride in two ways, depending on the reaction conditions. References 5 (Russian)  
[196-83440972]

UDC 546.18

1,2-BIS[1-(2,2,6,6-TETRAMETHYLPIPERIDINO)]DIPHOSPHENE

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 5 Jul 83) pp 465-466

ROMANENKO, V. D., KLEBANSKIY, Ye. O., SHUL'GIN, V. F. and MARKOVSKIY, L. N., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A new approach to the preparation of stable compounds of double coordinated phosphorus having a P=P bond is described using 1,2-bis[1-(2,2,6,6-tetramethylpiperidino)]diphosphene by treating 2,2,6,6-tetramethylpiperidinodichlorophosphine with an equimolecular quantity of bis(trimethylsilyl)mercury. References 4 (Western).  
[196-83440972]

UDC 547.241

STERICALLY HINDERED AMIDES OF PHOSPHONIC ACIDS AND SOME OF THEIR HETERO-ORGANIC DERIVATIVES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 4 Jul 83) pp 469-470

VEYTS, Yu. A., GUROV, M. B., DOMNIKOV, A. P., FOSS, V. L. and LUTSENKO, I. F.

[Abstract] By passing an excess of oxygen through a tetrahydrofuran solution of the lithium derivative of the ter-butylamide of di-ter-butylphosphonous acid followed by acidification with acetic acid, the ter-butylamide of di-ter-butylphosphonic acid was obtained at 90% yield. The ter-butylamide of diisopropylphosphonic acid was isolated by distillation after acetic acid acidification of the lithium salt of this amide. Condensation of lithium derivatives of these amides with acid chlorides of elements results in derivatives of various structure, depending on the nature of the element. References 2 (Russian).

[196-83440972]

UDC 547.282+547.241+547.46'052

REACTIONS OF 0,0-DIALKYLDITHIO ACIDS OF PHOSPHORUS WITH TETRACYANOALKANONES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 5 May 83) pp 470-471

NASAKIN, O. Ye., NIKOLAYEV, Ye. G., TERENT'YEV, P. B., BULAY, A. Kh. and KHASKIN, B. A., Chuvash State University imeni I. N. Ulyanov, Cheboksary

[Abstract] It was shown previously that 0,0-dialkyl(aryl)dithiophosphoric acids react with nitriles in the presence of water and acids to form thiophosphoryl compounds and thioamides. The same acids also react with tetracyanoalkanones in 2-propanol to form a number of products including dithiophosphites at 6-32 percent yield. References 4 (Russian).

[196-83440972]

UDC 547.26'118+547.745

TWO DIRECTIONS OF REACTIONS OF N-( $\omega$ -CHLOROALKYL)-2-PYRROLIDONES WITH TRIETHYLPHOSPHITE

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 19 May 83) pp 471-472

GUREVICH, P. A., KISELEV, V. V., MOSKVA, V. V. and MOSKVA, N. A., Kazan Chemical Engineering Institute imeni S. M. Kirov

[Abstract] It was found that the reaction of N-( $\alpha$ -,  $\beta$ -, and  $\gamma$ -chloroalkyl)-2-pyrrolidones react with triethylphosphite in two different directions. Thus, N-chloromethyl-2-pyrrolidone reacts with triethylphosphite via the classical Arbuzov reaction to form the phosphonate, N-(0,0-diethylphosphonatoyl)-methyl-2-pyrrolidone. However, N-( $\beta$ -chloroethyl)-2-pyrrolidone and N-( $\gamma$ -chloropropyl)-2-pyrrolidone react with the same phosphite to form the corresponding  $\beta$ - and  $\gamma$ -(N-pyrrolidone-2-yl)alkylphosphites instead of the expected pyrrolidone-substituted phosphonates. References 1 (Russian). [196-83440972]

UDC 547.241+547.118

VINYLTIOCHLOROPHOSPHORANES

Leningrad ZHURNAL OБSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 11 Apr 83) pp 473-474

DANCHENKO, M. N. and SINITSA, A. D., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] While the synthesis and properties of thiovinylic derivatives of tri- and tetra-coordinated phosphorus compounds are well known, little has been published on penta-coordinated phosphorus compounds containing the thiovinylic group. The authors prepared the first known vinylthioclorophosphoranes by chlorination of thiovinylypyrocatechinphosphites. These phosphoranes decompose partially during vacuum distillation to form pyrocatechinchlorophosphite and methyldithiocloroisobutyrate. Hydrolysis of the phosphorane with the precomputed amount of water in the presence of triethylamine results in methyldithiocloroisobutyrate and pyrocatechinchlorophosphite, as well as thiovinylyphosphite. References 3 (Russian). [196-83440972]

UDC 547.332+546.185.131

REACTION OF SUBSTITUTED  $\alpha$ -NITROOLEFINS WITH PHOSPHORUS PENTACHLORIDE

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 54, No 2, Feb 84 (manuscript received 6 Jul 83) pp 474-475

FAKHRUTDINOV, R. Z., RYABOVA, L. Ye., ARKHIPOVA, T. A. and MUSINA, R. G., Kazan Chemical Engineering Institute imeni S. M. Kirov

[Abstract] It was previously shown that  $\alpha$ -nitroolefins react with phosphorus pentachloride to form a complex which decomposes to form 1,2-dichloroalkyloximephosphoric acid chloride. The direction of this reaction depends on the nature of the substituent at the  $\alpha$ - and  $\beta$ -carbon atoms of the  $\alpha$ -nitroolefin. If a methyl group is present in the  $\alpha$ -position, a dichloronitrosoalkane is formed with the release of phosphorus chloroxide. Phosphorus pentachloride reacts with 2-nitro-2-butene to form 2,3-dichloro-3-nitrosobutane, also releasing phosphorus chloride. References 1 (Russian). [196-83440972]

PESTICIDES

UDC 547.288:615.777

USING MELDRUM'S ACIDS IN SYNTHESIS OF LOW MOLECULAR WEIGHT BIOREGULATORS,  
PART 1: SYNTHESIS OF NATURAL METHYLALKYLKETONES WHICH ARE CONTACT TOXINS  
FOR INSECTS

Moscow BICORGANICHESKAYA KHIMIYA in Russian Vol 10, No 1, Jan 84 (manu-  
script received 27 May 83) pp 100-103]

YEMEL'ANOVA, T. P., SEGAL', G. M. and TORGOV, I. V., Institute of Bio-  
organic Chemistry imeni M. M. Shemyakin, USSR Academy of Sciences, Moscow

[Abstract] Many wild plants have developed, by evolution, a resistance to insects. These natural insecticides were identified as ecdisones, anti-juvenile hormones, pyretrins, terpenes, etc. Recently, a mixture of ethyl-alkyl ketones containing mainly tridecane-2-one was extracted from the leaves of a wild tomato plant, *Lycopersicum hirsutum*, that is highly resistant to insects. Until now, ketones of this type were obtained chiefly by alkylation of acetoacetic ester subsequently splitting off the ketone. However, as the length of the alkyl chain is increased, the yield drops off markedly. In the present work, methylalkyl ketones of this type were prepared by alkylation of 2,2-dimethyl-1,3-dioxane-4,6-dione, Meldrum's acids. The resulting 5-acyl derivatives are readily hydrolyzed with acids and then decarboxylated to form the desired end product. A table gives the yields (48-85 percent) and physical constants for 16 ketones. References 25:  
1 Russian, 24 Western.  
[142-83440972]

## PETROLEUM PROCESSING TECHNOLOGY

### COLLOID CHEMISTRY OF PETROLEUM AND PETROLEUM PRODUCTS

Moscow KOLLOIDNAYA KHIMIYA NEFTI I NEFTEPRODUKTOV (NOVOYE V ZHIZNI, NAUKE, TEKHNIKE: SERIYA "KHIMIYA") in Russian No 2, Feb 84 pp 2-4, 63

[Annotation, introduction and table of contents of book by G. I. Fuks (deceased) "Colloid Chemistry of Petroleum and Petroleum Products", Izdatel'stvo "Znaniye", 26, 810 copies, 63 pages]

#### [Text] Annotation

With the development of chemical science and industry, petroleum and petroleum products (fuel, lubrication materials, stable hydrocarbons, etc.) have an ever-broader application in the economy. In this brochure the colloid-chemical fundamentals of these most interesting processes of oil extraction, industry and the application of petroleum products are examined.

The publication is addressed to lecturers, teachers and auditors of popular universities, to all interested in this important branch of chemical science and industry.

#### Introduction

It is difficult to imagine contemporary industry, agriculture and even the daily life of man without the automobile, airplane, tractor, metal machine tool, clocks and many other machines, mechanisms and appliances. All these objects could not work or, in any case, could not function reliably for any length of time without petroleum products. It is possible to produce a long list of materials that are composed of the products of the refining of petroleum or their derivatives. The residue of petroleum, fuel oil, is still widely used as a fuel. On the whole this signifies the exceptional value of petroleum and petroleum products for the economy. The amount of extracted oil is very great and in our country exceeds 600 million tons per year. In addition to this, the supplies of petroleum in the earth's core are substantial, but by no means limitless.

The intensification of the extraction of petroleum, the extraction of as much of it as possible from deposits, the improvement of refining, the increase of the output of valuable products and their quality, the rational selection and application of petroleum products, are important tasks of

scientific-technical progress. The solution of these problems depends on a series of disciplines of contemporary physical chemistry. Such fields of science as the physics of petroleum layers, petroleum chemistry and others have appeared some time ago.

For the past 10 to 15 years at the junction of the problems of petroleum and petroleum refining industry and the application of petroleum products, on the one hand, and colloid chemistry on the other, a new branch of knowledge has begun to be formed--colloid chemistry of petroleum and petroleum products. Contemporary colloid chemistry is the physical chemistry of surface phenomena and dispersed systems. In the early days of the development of petroleum industry, various phenomena and processes which relate to colloidal chemistry were already being examined (especially in the book by L. G. Gurvich "The Scientific Bases of Petroleum Refining", written in the beginning of the 1920's) but only recently has our knowledge begun to be put together in a defined system, necessary for separating a new field of science.

It has become clear that dispersed systems and surface phenomena play a significant role in the extraction, transportation and refining of petroleum. Many petroleum products, for example, asphalt and plastic lubricants, are such systems. The application of the laws of colloidal chemistry in production and of the use of petroleum products permits the essential improvement of their properties and elevation of quality. Significant possibilities for reducing the expense of petroleum products have also arisen.

In this brochure we will examine several fundamental aspects of colloid chemistry, we will give the characteristics of petroleum and petroleum products as dispersed systems and we will describe the volumetric and surface properties of dispersed petroleum products that lie at the basis of their application; we will also focus on the colloid-chemical foundation for improving the quality of petroleum products. On the whole, this will give the reader the possibility of obtaining an idea about the fundamentals of this new field of knowledge--the colloid chemistry of petroleum and petroleum products.

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CSO: 1841/188

UDC 547.582.3:542.924:547.26'118

REACTION OF DITHIO ACIDS OF PHOSPHORUS WITH CUMENE HYDROPEROXIDE

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received 28 May 82) pp 76-81

CHERKASOVA, O. A., MUKMENEVA, N. A., CHEBOTAREVA, E. G., OVCHINNIKOV, V. V., POBEDIMSKIY, D. G. and KIRPICHNIKOV, P. A., Kazan Chemical Engineering Institute

[Abstract] Breakdown reactions of cumene hydroperoxide by metallic dialkyldithiophosphates are well known. The high reactivity of the latter is assumed to be due to the formation of intermediate acid dithiophosphates which are active with hydroperoxides. In the present work, the stoichiometry of cumene hydroperoxide with dithiophosphoric acids was established. One molecule of the dithio acid ruptures 7,000 to 25,000 molecules of hydroperoxide. It was further established that the reactions proceed in a parallel manner through radical and nonradical mechanisms. The cessation of catalytic activity by phosphorus dithio acids is related to their capability to enter secondary reactions with the primary reaction products. Figures 2; references 13: 10 Russian, 3 Western.

[198-83440972]

UDC 665.74/75:542.943.7

KINETICS OF METALLIC COPPER CATALYZED DECOMPOSITION OF HYDROPEROXIDES FORMED DURING OXIDATION OF JET FUEL

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received 16 Mar 82) pp 82-85

GERASIMOVA, A. V., ZVEREVA, N. S., KOVALEV, G. I. and DENISOV, Ye. T.

[Abstract] Jet fuel, both during storage and in the engine's fuel system, is in contact with various construction materials. Also, soluble metallic compounds may enter the fuel as contaminants. These metals act as catalysts in oxidizing the fuel. To determine the inhibition mechanism when antioxidants are added, a study was made of the kinetics of the catalytic decomposition of hydroperoxides in T-6 jet fuel in the presence of copper and ionol antioxidant. It was found that a copper surface accelerates hydroperoxide decomposition in T-6 jet fuel. The decomposition rate constant is nonlinearly related to the surface area of the copper. Ionol inhibits hydroperoxide decomposition in concentrations less than  $2 \cdot 10^{-3}$  mole/liter. At higher concentrations the ionol is oxidized by the peroxides on the copper surface. Figures 5; references 2 (Russian).

[198-83440972]

CATALYTIC OXIDATION OF SULFIDES IN 190-360°C DISTILLATES OF CRUDE OILS INTO SULFOXIDES WITH AIR OXYGEN

Moscow NEFTEKHIMIYA in Russian Vol 24, No 1, Jan-Feb 84 (manuscript received 10 Jun 82) pp 106-114

MASHKINA, A. V., SHARIPOV, A. Kh., LYAPINA, N. K., MASAGUTOV, R. M. and SULEYMANOVA, Z. A., Institute of Catalysis, Siberian Department, USSR Academy of Sciences, Novosibirsk; Scientific Research Institute of Petrochemical Production, Ufa; Institute of Chemistry, Bashkir Branch, USSR Academy of Sciences, Ufa

[Abstract] Previous studies have shown that petroleum sulfides can be oxidized to sulfoxides in the presence of cuprous chloride and a solvent such as acetic acid. However, side product contamination and corrosion resulted with acetic acid as solvent, and isopropyl alcohol lowered the activity of the catalyst. In the present work, a study was made of the air oxidation of middle distillate fractions from various crudes with cuprous chloride in acetone as catalyst. This catalyst system was shown to be highly effective. At 80 mole % sulfoxide yield, the catalyst selectivity was 100%, which the productivity was 250 moles of sulfoxide per gram atom of copper per hour, which is two orders higher than that of other solvents. The oxidation kinetics of the sulfides over various copper catalysts are the same. The presence of thiophenes or hydrocarbons have little effect on the oxidation of the sulfides in the presence of the cuprous chloride-acetone catalyst system. Direct oxidation without extraction of the sulfur compounds appears to be the most advantageous. Figures 4; references 12 (Russian).

[198-83440972]

PHARMACOLOGY AND TOXICOLOGY

UDC 615.849.2.015.25.012.1

SYNTHESIS, COMPLEX FORMING PROPERTIES AND ANTIDOTAL ACTIVITY OF  
N'-ALLYLOXYETHYLENETRIAMINE-N,N,N",N"-TETRACETIC ACID

Moscow KHMICO-FARMATSEVTICHESKIY ZHURNAL in Russian No 2, Feb 84 (manu-  
script received 22 Apr 83) pp 166-170

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[Abstract] The hydroxyethyl analog of diethylenetriamine-N,N,N',N",N"-pentacetic acid (I) was synthesized in a previous work and it was found that its trisodium calcium salt may be used as an antidote for a number of toxic metals. In the present work, the allyl ester of (I), N'-allyloxyethylene-diethylenetriamine-N,N,N",N"-tetracetic acid (II) was prepared and its antidotal properties were studied. Biological tests on white rats showed that complexon II forms stable complexes with Mg, alkaline earth metals, transition elements, Eu and Y. However, it did not surpass complexon (I) with respect to rapid elimination of  $PU^{239}$  from the body. Figures 2; references 12: 7 Russian, 5 Western.

[186-83440972]

UDC 615.281:547.558.1].012.1

ANTIMICROBIAL PROPERTIES OF SOME HETEROCYCLIC COMPOUNDS AND CHLOROMETHYL-  
 $\beta$ -ARYLAMINOVINYLKETONES

Moscow KHMICO-FARMATSEVTICHESKIY ZHURNAL in Russian No 2, Feb 84 (manu-  
script received 25 Jul 83) pp 173-175

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[Abstract] A study was made of the antimicrobial properties of substituted 1,2,3-triazoles, pyrazoles and isoxazoles. By reaction of chloromethyl- $\beta$ -chlorovinylketone with substituted phenylazides in benzene solution, three derivatives of 1-aryl-4-chloroacetyl-1,2,3-triazoles were synthesized.

Reaction of chloromethyl- $\beta$ -chlorovinyl ketone with diazomethane and hydroxylamine resulted in chloromethylpyrazolyl-2-ketone and 3-chloromethylisoxazole, respectively. Phenylhydrazine derivatives yielded 1-aryl-3-chloromethyl-pyrazoles. The first seven compounds were active against gram positive bacteria and antracoidal bacillus strain 297. The nature of the substituent on the phenyl ring affects both its microbial activity and its spectrum of action. References 9 (Russian).

[186-83440972]

UDC 615.281.8: [546.57+546.73].012.1

#### SYNTHESIS AND ANTIVIRAL ACTIVITY OF SILVER AND COBALT SALTS OF DERIVATIVES OF p-AMINOBENZENESULFONAMIDES

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 2, Feb 84 (manuscript received 16 May 83) pp 175-178

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[Abstract] Although the antimicrobial activity of cobalt and silver salts of certain derivatives of p-aminobenzenesulfamide are known, data are lacking on their antiviral activity. In the present work 12 silver and cobalt salts of p-aminobenzenesulfamide derivatives were synthesized and their antiviral activity tested against classical bird plague, Newcastle's disease, vesicular stomatitis, Venezuelan equine encephalomyelitis, herpes simplex vaccine and passive dermatomuscular human embryonic cells. None of the silver salts had antiviral activity, but almost all of the cobalt salts were active, suggesting that the multivalent nature of cobalt plays a role. References 20: 10 Russian, 10 Western.

[186-83440972]

UDC 615.917.036.11.07

#### PREDICTING ACUTE TOXICITY OF ORGANIC COMPOUNDS ON BASIS OF METHODS OF SAMPLE RECOGNITION

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 2, Feb 84 (manuscript received 8 Dec 83) pp 181-188

SOLOMINOVA, T. S., MAKSIMOV, G. G. and SEMENOV, V. A., Ufa Scientific Research Technological Institute of Herbicides and Plant Growth Regulators; Ufa Scientific Research Institute of Hygiene and Occupational Diseases

[Abstract] Three methods were studied for the possibility of predicting the acute toxicity of organic compounds by computer. The main component method

utilizes molecular weight, molecular refraction and molecular geometry, while the information-logic system (ILS) "Spectrum" searches and predicts toxicity on the basis of infra-red spectra. The OKAS algorithm is based on the structural fragments of the compound which are typically toxic. The method of main components developed to be the most practical. Figures 2; references 18: 15 Russian, 3 Western. [186-83440972]

UDC 615.2/.3.07:66.085.3

#### INCREASING MICROBIAL PURITY OF NONSTERILE MEDICATIONS, RAW MATERIALS AND AUXILIARY MATERIALS WITH ULTRAVIOLET LIGHT

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian No 2, Feb 84 (manuscript received 27 Apr 83) pp 209-213

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[Abstract] In the production of finished medications, the pharmaceutical industry is faced with the problem of the development of dependable control over microbial contamination of nonsterile medications during the production phase. One possible solution is the greater use of ultraviolet light. Although well known, its use is still not very widespread owing to the fact that only a very thin layer of material is sterilized due to the opacity of the material, and also the lack of dependable ultraviolet light sources of sufficient power. After listing its advantages, the authors recommend greater use of ultraviolet light during production of medications. Figures 1; references 25: 13 Russian, 12 Western.

[182-83440972]

## POLYMERS AND POLYMERIZATION

### POLYMERS AS SUBSTITUTES FOR METAL AND LUMBER

Moscow PLANOVYE KHOZYAYSTVO in Russian No 1, Jan 84 pp 109-113

[Article by A. Musifulin, sector chief in NIITEKHM [Scientific Research Institute for Chemical Economics], doctor of economic sciences: "Outlook on the Use of Polymer Materials"]

[Text] The development of productive strengths in recent decades posed the problem of adoption of new directions in technical progress and conversion to the use of highly effective materials, energy resources and progressive techniques and engineering. Metal, wood and other materials will more and more be replaced by economical, practical and light-weight synthetic materials.

In this decade in this country, plans have been made to carry out a broad system of measures for developing technical progress and increasing the effectiveness of national production, including reducing consumption of materials and energy of the national product based on a qualitative change in the structure of the material and fuel energy balance sheet and a decrease in the consumption of metals, energy, etc.

In the 11th Five-Year Plan it was specified: save 10.6 million tons of rolled ferrous iron (including 8.5 million tons in machine building and 2.1 million tons in construction), 205 million tons of conventional fuel,<sup>1</sup> accelerate significantly the development of the production of polymer materials possessing higher thermal stability, mechanical strength and other properties. The indicated amount of economy of metal and fuel-energy resources can be achieved both because of a lowering of the norm and accepted standards for the consumption of materials, energy and their optimum use and also because of the replacement of metals by other building materials based on the improvement of the structure of the material balance sheet.

The solution of many social-economic problems planned at the 26th Congress of the CPSU was linked, to a considerable degree, with the development of polymer chemistry and the introduction of chemical processes into the national economy. For industry, agriculture, construction and other branches, and also the output of modern consumer goods, wide use is required of new inexpensive synthetic materials with various properties assigned in advance. Successes achieved in the field of polymer chemistry in recent years permit such materials to be produced.

The production pattern of building materials is constantly changing due to the effect of chemistry. The characteristic property of such a change in recent years is such that, in the balance sheet of metals, the proportion of light-weight corrosion-resistant and high-strength metals and alloys is constantly increasing, and, in the balance sheet of building materials altogether, the proportion of polymers, plastics, resins and synthetic filled materials is also increasing.

An increase in the relative share of polymers is dependent, on the one hand, on the development of new, more advanced industries (the electronic, electrical engineering and radio engineering industry, instrument engineering, ship building, automobile manufacturing, aircraft construction, etc.) and, on the other hand, on the constant growth in demand for large-capacity polymer production: polymer pipes, film, consumer goods, clothing, footwear, furniture, household and cultural and personal articles, packaging, containers, etc. In spite of the fact that production of synthetic materials is developing extremely nonuniformly in different countries, specialists forecast a great outlook for them. According to forecasting data, the world production of polymers, chiefly synthetic resins and plastics, will comprise about 160 million tons by 1990.<sup>2</sup> Polymer bodies and frames of automobiles, all-plastic railroad cars and trains, sport and small-size passenger aircraft, etc., have already been planned in the most recent years of this century.

In our country due to deep penetration of polymers into different areas of national production, the rate of growth of metal funds has slowed down, metal content has decreased and the polymer content of the final product has increased. (In the last 10 years the proportion of consumption of metal per 1 million rubles of industrial production has decreased by 18-21 percent, and the relative proportion of synthetic resins, plastics and fibers grew by 20-22 percent.) The trend of the development of the economy of a number of countries shows that increasing amounts of the use of metals was mainly characteristic of the technology of former periods. With the emergence of new industries and productions, technological progress all the more became determined by the level of use of advanced building materials, including polymers.

In the total pattern of national production per unit of industrial production in the national economy, cast iron, steel and lumber are consumed 1.3-1.4 fold greater, and synthetic resins, fibers and plastics considerably less than in other countries which are advanced with respect to technology. A high level of use of metals and wood attests to the fact that Soviet industry up to now has principally developed on a base of using natural materials and traditional methods of mining and treatment, and this leads to growth in the intensiveness of consumption of natural resources. Under these conditions chemists in this country have been assigned the task of accelerated development of production of highly effective synthetic materials for building and other purposes and the solution of urgent problems in the field of the interchangeability of natural and synthetic materials.

The problem of the interchangeability of materials includes within it the solution not only of economic but also technical problems, inasmuch as

there lies at its base, on the one hand, the technical compatibility of the new and the old, natural and synthetic materials,<sup>3</sup> and, on the other hand, their social-economic effectiveness. If on the basis of technical compatibility the possibility develops of introduction of a new material, the expediency and necessity for its use in practice are determined on the basis of economic efficiency. But it would be erroneous to assume that modern polymers must necessarily replace metals and other materials. The necessity for production of synthetic materials is determined not by the fact that previously used metals and other traditional materials are obsolete, but by the fact that with the development of new sectors of the national economy by the acceleration of scientific-technical progress and by the necessity for solutions of many urgent social-economic tasks, a requirement arises for materials with new properties obtained with least costs for labor, energy and natural resources.

The amounts of replacement of metals, wood, concrete, glass and other materials by plastics up to the present time have not been large because of the latter. According to research results, at the present time more than 12 million tons of metal and about 28 million cubic meters of wood and lumber in this country are used in those areas where it is possible to use plastics and other synthetic materials (Table 1 and 2). This means that approximately 8 percent of the metal and 12 percent of lumber consumed in the national economy may be replaced by polymer materials. A considerable volume of the metal economy can be obtained by means of the use of polymers in the production of pipes, medical-technical articles and also steel pipes and elements of pipelines lined with polymers.<sup>4</sup> Polymer pipes are widely used in different areas with a high economic effect. The advantage of polymer pipes over metal is, first of all, in their high resistance to corrosion, light weight, low thermal conductivity and coefficient of friction and, in the second place, they have a relatively low price and require lower expenditure of energy, labor, capital outlays and natural mineral resources to produce them. To satisfy the demand in the areas indicated for such pipes, 1.13 million tons of synthetic resins and plastics are required instead of 7.1 million tons of metals.

Very scarce, very costly metals can be saved by the use of polymers as building materials in machine building. Sectors of machine building need in all 315-320 thousand tons of construction plastics instead of 1.7 million tons of ferrous and nonferrous metals with an average coefficient of substitution of materials of 5.3. While in the production of pipes and medical-technical articles, relatively inexpensive polymers are required, in machine building, as a rule, high-quality construction polymers with definite service properties are required (glass-fiber plastics, polyamides, polycarbonates, "ABC plastics" and others). In spite of the fact that these polymers are costly, the effectiveness of their use instead of metals here is 1.4-1.6 fold higher than in other sectors of the national economy.

A very great volume of wood and lumber can be saved by the use of plastics, synthetic resins and molded materials in the construction and furniture industries and also in the field of the production of packaging and containers. About 1 million tons of plastics and synthetic resins instead of

Table 1. Amount of Possible Saving of Metal Because of the Use of Polymer Materials

Field of Use of Polymer Replacing Metals	Amount of Replaced Materials, millions of tons	Average Coefficient of Exchange of Metals	Economic Effectiveness from Reduction of Costs, millions of rubles
Plastics, Synthetic Resins and Molded Materials			
Production of Pipes and Their Insulation	0.94	5.70	670
Production of Fittings and Other Elements of Pipe-lines	0.06	0.30	55
Production of Medical-Technical Units and Equipment	0.13	1.10	90
Machine Building Including Manufacture of Automobiles	0.32	1.70	360
Furniture Production	0.18	0.90	---
Production of Packaging and Containers	0.04	0.20	3
Transport	0.11	0.60	85
Repair-Maintenance and Other Needs	0.07	0.40	7
Total	0.43	2.00	350
	2.1	12.0	1620

Table 2. Amount of Possible Saving of Lumber Because of the Use of Plastics and Synthetic Resins

Field of Use of Polymers as a Substitute for Lumber	Amount of Materials Substituted			Economic Effectiveness from Lowering of Costs, millions of rubles
	Plastics and Synthetic Resins, thousands of tons	Lumber, millions of cubic meters	Average* Coefficient of Substitution of Materials	
Capital Construction	420	13	15	205
Production of Packaging and Containers	390	7	9	270
Furniture Production	170	3	11	115
Cellulose-Paper and Wood-Working Industry	60	1	8	45
Repair-Maintenance Needs	90	2	12	50
Other Areas	130	2	9	55
<b>Total</b>	<b>1260</b>	<b>28</b>	<b>12</b>	<b>740</b>

\*For the calculation of the substitution coefficient, wood is converted from cubic meters into tons.

23 million cubic meters of wood are required to satisfy the demand of these sectors of the national economy. The highest substitution coefficients for lumber are achieved by the use of synthetic materials in construction for production of shaped-turned out articles of different construction designs, and also floor boards, as well as for the production of some forms of packaging, containers, bottles, boxes, etc. A very economical effect from the use of polymers is possible in the furniture industry, and several sectors of transport machine building and instrument building. In the future, the wood economy may increase considerably because of more extensive chemical treatment of lumber and its by-products and wide use of highly-effective chemical processes in the wood-treating industry.

It should be noted that modern polymers are used effectively as building materials in many technically developed countries. Thus for machine-building needs, the United States uses more than 2.6 million tons of synthetic resins and plastics. Of them about 49 percent is directed toward electronic and electrical engineering production and 35-36 percent for output of automobiles and other means of transport.<sup>5</sup> In addition, more than 1.4 million tons of polymers are used for pipe production. This amount of pipes is approximately equivalent to 8 million tons of metal pipes. To satisfy the demand of construction, 3.4-3.5 million tons of synthetic resins and plastics, about 330 million square meters of planed wood boards and more than 1,800 million cubic meters of plywood are used annually. In addition, more than 4 million tons of synthetic resins and plastics are used for production of polymer packaging and containers.<sup>6</sup> According to our calculations this amount of polymers is equivalent to 35-40 million cubic meters of lumber.

Glass, concrete, ceramics, resins, paper, cotton cloth and other materials can be replaced by polymers in large volume. The field of possible use of polymers is constantly increasing in proportion to the expansion of the assortment of plastics produced, the improvement in their quality and also acceleration of the rates of production of polymer-containing designs of machines, instruments and consumer goods. To satisfy economically effective demands of the national economy, more than 10 million tons of synthetic resins, plastics and chemical fibers are required at the present time. At the same time it is necessary to increase the quality and coefficient of useful life of polymer materials and to use more widely high-coefficient fillers for plastics. Only by an increase in the coefficient of useful life of the majority of thermoplastics in machine building up to standard (0.94-0.98 instead of 0.85-0.86) will the resources of plastics be able to increase to 320-350 thousand tons.

A considerable increase in the production of polymers (approximately by 1-1.1 million tons) is possible to achieve because of the redistribution of capital means, and, in the process, metals which they replace are saved. To produce and process 1 million tons of construction polymers requires a capital expenditure on the average of 1.2-1.3 billion rubles less than for the equivalent amount of metals. With an increase in the coefficient of useful life of polymers the value of the economy indicated above comprises about 1.5 billion rubles.

It is also possible to broaden the production of polymer materials because of redistribution of capital outlays within the chemical industry. A large part of the capital outlays in this sector in recent years was directed toward an increase in the output of mineral fertilizers. As the result our country leads the other countries of the world in volume of production of chemical fertilizers. But for a number of reasons annual losses of fertilizers are considerable. Thus, just in transport from plants to fields they comprise 11.5-14 percent.<sup>7</sup> One of the reasons for this is the shortage of proper packaging, polymer film materials for packing, transport and storage of fertilizers. According to our calculations 65-70 thousand tons of film materials are necessary, for production of which 140 million rubles of capital outlay and 75-80 thousand tons of hydrocarbon raw material are needed. A lowering of losses, determined by a given factor, by 40-50 percent would permit the saving of more than 1.8 billion rubles. Such a sum is sufficient to increase the capacity for production of polymer materials by 1.5 million tons.

In addition, one should take into account that because of the growth of production volumes and improvement in production quality in the polymer industry there are considerably greater possibilities for a rise in labor productivity, a reduction in production costs and capital intensiveness than in sectors producing metals and other traditional materials. As it is evident from the data presented, real possibilities for development of production of polymer materials in our country are great, and it is necessary to make use of them. This would permit not only an increase in the economic effectiveness of public production but also the moderation of material, fuel-energy and ecological pressure.

According to their physical-chemical properties and characteristics, modern plastics are the most universal and at the same time most economically effective building materials. Their effectiveness is shown, in the first place, in the fact that many useful properties of these materials in the production process are obtained with the least expenditure for national labor, and in the second place, they require less expenditure for energy, raw materials and capital outlays for processing into articles. It was established that at the production step many useful properties which are included in polymers used in manufacturing are 9-12 times cheaper in comparison with nonferrous metals and 1.5 times cheaper in comparison with ferrous.<sup>8</sup>

However, the interchangeability of natural and synthetic materials must be determined not only by the comparability of cost indexes but also by the volumes of expenditures for natural raw materials and energy for their production, because minimization of the indicated expenditures for the product does not always conform to minimization of expenditures for natural resources. Meanwhile under conditions of increasing shortages of mineral raw material and fuel it is necessary to be concerned economically not only with expenditures for living labor but also for natural resources.

With the existing technology for production and processing of 1 ton of plastic the input of fuel-energy and mineral resources is 1.4-1.5-fold and the input of fresh water and oxygen is 2-4-fold less than for the production

of an equivalent amount of ferrous and nonferrous metals, at the same time 3-4-fold fewer harmful substances contaminating the environment are formed, and 5-7-fold less industrial wastes. This permits an effective solution not only of economic but also social problems, and above all, ecological problems.

Therefore, to obtain 1 ton of gasoline today an average of 2.5-3.5 tons of oil is expended (depending on the level of development of the country). At the same time 1 ton of gasoline (cost 60-80 rubles) can be used as a fuel for automobiles or for the production of 0.3 ton of polyethylene (cost 220-240 rubles), which can replace about 2 tons of ferrous and nonferrous metals or more than 4 cubic meters of lumber. In order to obtain the indicated amount of ferrous metals, it is necessary to extract them from the depths of the earth and process not less than 5-7 tons of ore, coal and other forms of raw material, and in order to obtain the same amount of nonferrous metals it is necessary to process more than 70 tons of ore and mineral raw material. By comparison of these data it is not difficult to be convinced that for the production of an equivalent amount of polymers not only is less living labor required, but also fewer natural mineral resources. Such an analysis of expenditures should lead not only to the stage of obtaining interchangeable (natural and synthetic) materials, but also to the stage of their processing and the output of the final product and also to their use by the consumer.

As the results of study show, the use, in manufacturing, of polymers instead of metals even today can save more than 10 million tons of steel and cast iron and several thousand units of metal-treating equipment; labor costs can be reduced by 300 thousand men, 12.5-13 billion KWH of electrical energy can be economized and 4.5-5 billion rubles of capital outlay can be saved. A large part of the indicated economy of labor and energy and capital expenditures are achieved at the stage of processing the polymers, chiefly due to reduction of the amount of mechanical treatment. Considerable economy is also achieved at the use stage, directly by the consumer of polymer articles. Calculations show that the use of polymer materials as a substitute for ferrous and nonferrous metals contributes to a lowering of the material mass (of automobiles, ships, railroad cars and other means of transport) by 3.2-3.5 million tons and permits an economy because of this factor up to 450-500 thousand tons of fuel calculated on petroleum. This amount of petroleum product is sufficient for supplementary output of 40-45 thousand tons of plastics and synthetic resins.

The importance of modern polymers appears not only in lowering labor, energy and natural resources, reduction of production waste products and atmospheric contamination, but also in qualitatively new properties conferred by them to production. Their use in the manufacture of automobiles, refrigerators, furniture or other merchandise for consumer use makes the articles lighter, more durable, more decorative, more esthetic and more comfortable--in a word--modern. In addition, due to their properties, polymers show a definite influence on the perfection of heavy labor-consuming production processes and the improvement of working conditions and safety technology.

In spite of the fact that the first polymers actively entered our life more than a quarter of a century ago, up to now they have occupied a modest place in the structure of the material balance of the country. For many years, in the development of the metallurgical industry, people studied how to employ effectively the useful properties of metals and their alloys; the properties of polymer materials are still not used in a sufficiently innovative way. As a result, a large part of plastics resources are used ineffectively in old, previously mastered areas. The introduction of chemical processes into the national economy until now has not shown a proper influence either on accelerating the pace of technical progress or on increasing the effectiveness of national production.

In recent years, under the influence of scientific-technical progress in chemistry, deterioration in standards for several forms of previously mastered polymers has accelerated; the relative level of the quality of synthetic materials produced has lowered in comparison to world standards. The progressiveness and the reliability of technology of the future to a considerable degree are predetermined by today's state of development of production of improved materials, and most of all, of polymers. To overcome deficiencies in this area, considerably more energy and time will be required tomorrow than is set aside for them today. Therefore, it is necessary to pay serious attention to polymer chemistry, accelerate the tempo and perfect the structure and direction of development of the plastics industry, and, in a practical and innovative way, solve contemporary problems of the introduction of chemical processes into the national economy.

#### FOOTNOTES

1. N. Baybakov, "The 11th Five-Year Plan, Its Features and Tasks." PLANOVYE KHOZYAYSTVO No 1, 1982, p 6
2. BYULLETEN' INOSTRANNOY KOMMERCHESKOY INFORMATSII, 1980, No 105, p 6
3. The technical compatibility of materials is determined in the process of analysis and comparison of the physical and chemical properties of the old and new materials.
4. More than 20 million tons of metal are required annually for production of pipes and medical-technical articles. However, in the process of their use the strength properties are only 25-30 percent used. At the same time because of corrosion the life of metal pipes is 3-4 fold shorter than polymer pipes.
5. See the series KHIMICHESKAYA PROMYSHLENNOST' ZA RUBEZHOM OBZORNAYA INFORMATSIYA, No 8. Moscow, NIITEKHIM, 1981, p 16
6. Ibid, p 15
7. See KHIMIYA V SEL'SKOM KHOZYAYSTVE, 1977, No 1, p 3-6

8. The specific costs per unit of basic properties of materials (friction resistance, corrosion resistance, strength, etc.) are determined by the ratio of the costs of metals and plastics and their physical-chemical parameters.

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CSO: 1841/152

## POLYACETYLENE AND K

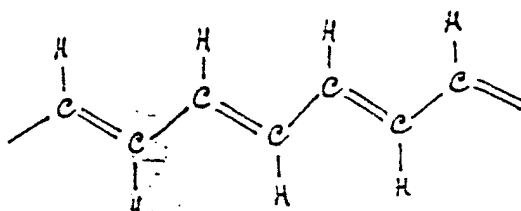
Moscow KHIMIYA I ZHIZN' in Russian No 3, Mar 84 pp 23-28

[Article by V. Mishin]

[Text] In conjunction with the word "semiconductor," silicon and germanium figure much more often than the substances about which we are talking here. Silicon and germanium are indeed the most important materials of electronic engineering. But, after all, there are more semiconductors among organic substances than among inorganic. On the whole there are hundreds of thousands. However, for the majority of such substances, conductivity is an insignificant property which has not been reflected in their practical fate, while electrical conductivity of polyacetylenes has been studied by chemists for 3 decades now. All of the new polymers of this series are being synthesized and, now, polyacetylene and its derivatives are already being tested for use instead of selenium in xerography, instead of graphite in brush-bushing-electrodes of electric motors, instead of silver in photography, instead of silicon in solar batteries and instead of lead in batteries. And who knows what the future holds.

### Conjugation

The polyacetylene molecule is an example of a very simple polymeric structure. It is a little chain of carbon atoms, which forms during the polymerization of acetylene, when in the  $\text{CH}\equiv\text{CH}$  molecule, one bond is broken.



The distribution of these very atoms is conveyed precisely enough in this scheme, although it says nothing of the distribution of electrons in the molecule. The scheme is not well defined: single and double bonds can be

exchanged in places and the molecule will stay the same. In reality, not entirely. Double bonds are formed by  $\pi$ -electrons, whose orbits are located outside the surface of the molecule, over and under it. Such bonds are called conjugated. A conjugated bond cannot be considered localized, belonging to two atoms. Orbita of  $\pi$ -electrons of adjacent atoms overlap, and a single electronic cloud of a polymeric molecule forms. It is attached rather weakly to the shell of the chain. The role of the wind which causes the cloud to move (and the polymer to conduct the electric current) is played by the electric field. It is important that these clouds are "going broadside" to the wind: at any direction of the electric field, they move strictly along the ionic shell. Conductivity of the polymer along the molecule is much more than crosswise. And if the entire story of properties of polyacetylene and its derivatives had to be reduced to one word, then that word would be "conjugation."

#### Synthesis in the Church Lodge

The history of polyacetylene began in the setting of the former Moscow Church of the Sign, which is located at the Petrovskiy Gates. In the 50's, the Laboratory of Anisotropic Structures of the USSR Academy of Sciences was located there, and when in 1958, N. N. Semenov became its director, organic chemists appeared in the former church. However, the first synthesis of organic polymers with semiconducting properties were not even held in the church itself, but in the church lodge: the work was clearly not paramount for the laboratory. In a year, it is true, this research was continued at the Institute of Chemical Physics of the USSR Academy of Sciences, and 10 years later, a special laboratory of the chemistry of photo and semiconducting polymers was organized in the institute. It is directed by M. I. Cherkashin, presently a doctor of chemical sciences, but then, in 1958, a young candidate, who was commissioned to synthesize polymers with conjugated bonds.\*

The original monomer for the first synthesis was phenylacetylene  $C_6H_5C\equiv H$ , which differed from acetylene in that one hydrogen atom in the molecule was replaced by a phenyl ring



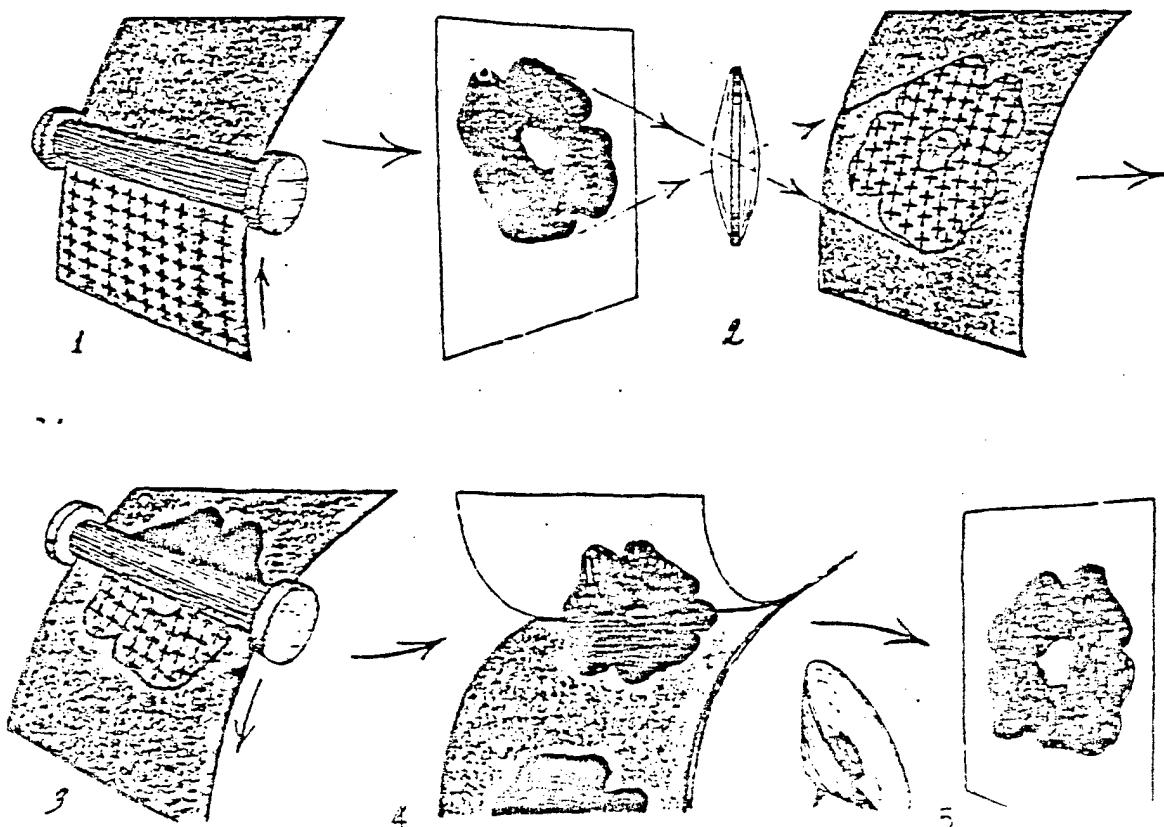
of the benzene molecule

without one hydrogen atom. Benzene (and the phenyl-radical too) can be viewed as a trimer of acetylene; there are also conjugated bonds in them. Thus, each phenyl ring adds a small cloud to the general electronic cloud of the polymeric molecule, and this increases the polymer's conductivity. This, as a matter of fact, also caused the original monomer to be chosen. First of all, it was necessary to purify the monomer. This was done, and one day the solution of phenylacetylene, which was carefully purified and heated to 150°C, was left overnight in the laboratory. In the morning, a viscous mass was observed in it: polymerization proceeded without any catalysts at all.

\*Then, 20 years ago, the study of organic semiconductors of different classes began practically simultaneously in several laboratories of this country.

Similar surprises, in general, are not so rare in laboratory practice--the first polyethylene was also produced accidentally. But polyphenylacetylene continued to be a further surprise. It is an ordinary matter to draw metal from a solution with electrolysis. It turned out that electrolysis can also be used to draw out polyphenylacetylene. In solutions of some acids ( $CCl_3COOH$ ,  $HClO_4$ ), molecules if this polymer were charged: positively charged hydrogen atoms were attracted to  $\pi$ -electrons of the polymeric molecule, but due to conjugation, they sometimes preserved free movement--only along the polymeric chain. In the electric field, hydrogen ions were displaced along the chain, they reached the end of the polymeric molecule and began to pull it toward the anode. A polymeric film, in which molecules set themselves up perpendicular to the surface of the electrode, gradually formed on the anode.

The film was received in good order, almost crystalline, and its electric resistance was  $10^{14}$  times less than for the poorly regulated polymer-- $10^2 \Omega \text{cm}^{-1}$ . During one of the experiments, the polymeric film on the anode grew, and continued to grow to the cathode--this shortened the chain and disabled the entire arrangement. But that was in another institute. Coworkers of "Khimfizika," knowing the peculiarities of the new polymer, could not allow this.



[Explanation of figure on next page]

Basic stages of the xerographic process: semiconductor layer is charged (1) and exposed; the charges, running out from the illuminated sections, create a hidden image (2); then the image is revealed with a charged resin powder (3), the image is transferred to preliminarily charged paper (4) and, finally, the image is fixed, fusing the resin powder (5).

#### Width of Forbidden Zone

The synthesized polymer turned out to be a semiconductor and much closer in properties to regular inorganic than to other organic semiconductors. The most important characteristic of such materials is the width of the forbidden zone. The electron must overcome it in order to fall into the conductivity zone and become a charge transmitter. The smaller the width of the forbidden zone, the higher the conductivity. And so the width of the forbidden zone for polyacetylenes amounts to approximately eV, as for silicon. For the majority of organic semiconductors, the forbidden zone is wider, and, consequently, conductivity is lower.

With a rise in temperature, the number of electrons, transferred by heat impulses through the energy slit, grows--as does the conductivity of the semiconductor. A quantum of light can give energy, which is essential for overcoming the forbidden zone, to the electron, and the semiconductor's conductivity in the light increases. The work of photoelements and solar batteries is based on this effect. For regular inorganic semiconductors, the width of the forbidden zone and other most important characteristics have constant values. Semiconductor-polymers are another matter: their characteristics can be altered by many methods. It is possible to create new derivatives of polyacetylene, in which hydrogen is replaced by various radicals; it is possible to vary the conditions of polymerization, thereby changing the length of the polymeric chain; it is possible to stack the polymeric molecules into fibers and layers differently, changing the electric resistance in places of contact between molecules....

#### Appearance of the Hero

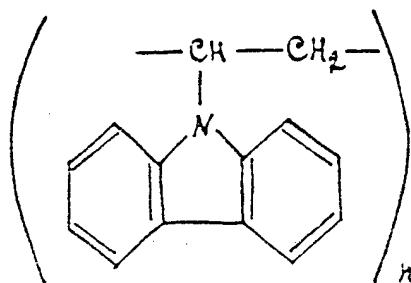
After the synthesis of polyphenylacetylene, polyacetylene itself was produced. However, in the very first experiments, its extreme instability was revealed. It was easily oxidized by atmospheric oxygen, and all of its semiconductor properties were lost--oxygen brought the effect of conjugation in the polymeric chain to nothing. The laboratory experiment could, of course, have been conducted in an atmosphere of inert gas, but then it was difficult to reply upon some sort of practical use for such an unstable substance. Among the derivatives of polyacetylene, there turned out to be sufficiently stable polymer-semiconductors, and research of polyacetylene itself was stopped for a long time. The story about why it was remembered 20 years later will be told at the end of the article, but now, on to those derivatives of polyacetylene which are already used instead of inorganic materials.

## Instead of Silver and Selenium

The depletion of silver resources is now being discussed often enough. Nevertheless, here too are a few figures. Strictly speaking, silver deposits on this planet are almost completely depleted; silver is extracted from ores of nonferrous metals, and ore with 3 grams of silver to a ton is considered profitable. Approximately a third of the silver obtained this way is now spent on the needs of the photograph and motion picture industry. Nonsilver motion picture-photo materials are being sought in various directions and with variable success. One of these directions has to do with organic semiconductors. The classic photoprocess on silver halides, of course, is universal, but not overly. It is awkward and slow in comparison to xerography--the most widespread method at the present of reproducing printed texts, manuscripts and illustrations. And, after all, xerography, in essence, is one of the forms of electrophotography. In xerography, photoconductivity of semiconductors (usually selenium) and a rise in their electrical conductivity under the influence of light are used. The charge is deposited on the layer of the semiconductor, after which an image is projected at this same layer--conductivity of the illuminated sections increases, and the charge "discharges" to the metallic under-layer. Then the black resin powder with an opposite charge "displays" an image, adhering to those sections of the semiconductor layer on which the charge was preserved. It remains to transfer the powder to the paper and to secure the image which fused the resin.

For a long time, numerous technical improvements in xerography did not affect the main item--the selenium semiconductor layer, although it has quite a few defects. In the first place, selenium is toxic. Secondly, only amorphous selenium has photoconductivity, and after some time it begins to crystallize. Thirdly, the selenium layer wears away fairly quickly, in so far as in each duplication cycle, special brushes pass over it, which brush off remains of the displaying powder. In all the life of selenium cylinders is calculated in thousands, in the best case, tens of thousands of copies.

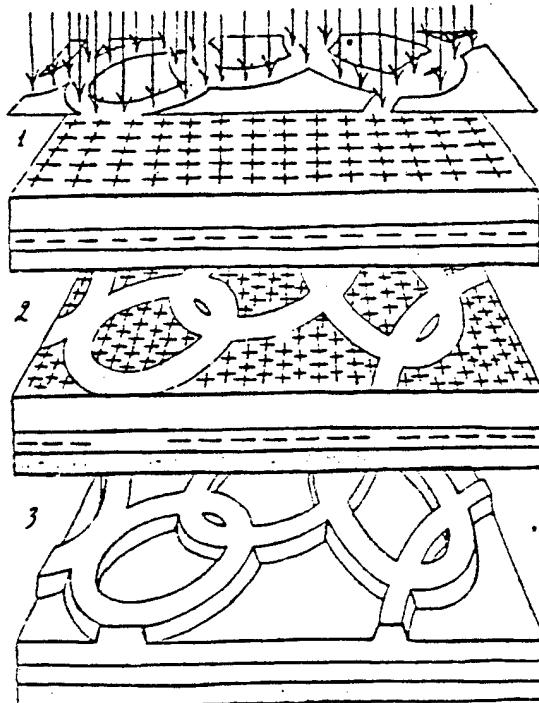
Many derivatives of polyacetylene could serve as polymeric replacements of selenium, if they are alloyed with acceptor additives. Much more convenient, available and inexpensive is poly-N-vinyl-carbozol:



The cloud of conjugated bonds of the carbazole nucleus can deservedly be termed swarms; however, the polymer does not conduct a current: there is

no bond between the clouds and conjugation is absent in the basic chain. The role of lightning is played by a quantum of light--it excites the electronic cloud, and under the influence of the electric field, the excited electrons are transferred from one carbazol nucleus to another. The polymer is fixed to the conducting under-layer, and the copying machine is immediately charged by an entire roll of such film. Now, when the semiconductor layer is wiped off (after several thousand copies have been received), it is necessary, as in a camera, to transfer the film to one "frame."

Microfilms are now also done by the xerox-copying method. A thin conducting layer of nickel and a photosensitive layer of the same polyvinylcarbazol is attached to the transparent lavsan base. The image is projected and fixed, as in ordinary electrophotography; the resin, as in xerography, is fused. The image remains on film forever. It is impossible to remove it, but it is possible to add something to it: for this it is necessary simply to repeat all stages of xerox-copying. The capability of materials with a polyacetylene derivative is 200 lines/mm. This is entirely sufficient for producing microfilms of normal quality.



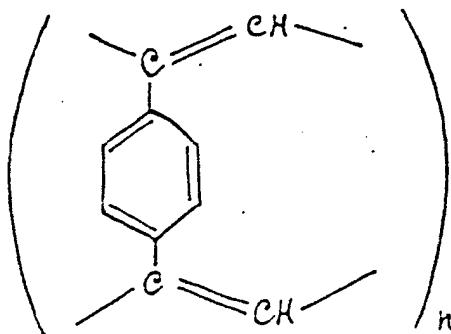
Record of the image on thermoplastic deformed layers: the charge is fixed on the surface of the photothermoplastic layer; an opposite charge is induced in the thin transparent metallic layer (1); after exposure, a hidden image is formed, and exactly the same distribution of charges remains in the metallic layer (2); when heated, the charged sections are attracted and make the image a contrasting relief (3), and subsequent cooling fixed the image.

The thermoplastic photoconducting layer of polyvinylcarbazol can be obtained another way: when the charged sections are heated, they are attracted to the conducting base, the film deforms and the relief on its surface becomes a carrier of information, which may be considered a simple optical system.

This method, which is called recording on thermoplastic deformed layers, has many advantages. In the first place, the image may be considered simultaneously with the recording, thereby controlling the quality of the record. In the second place, the processing of images is very simple (heated--it has appeared, cooled--it has been fixed). In the third place, the image may be wiped off by repeated heating, and the film will again be ready to record. Finally, in the fourth place, with the aid of thermoplastic deformed films, it is possible to obtain color images. This method is used in motion pictures and television, but very high hopes for it are held by specialists in the construction of input-output of information for computers. The recording may be carried out very quickly, with a laser beam for instance. The optical principle of recording renders a very large density of information. (Remember how many copper wires are replaced by one light conductor.) It is possible to record holograms, which are not harmed by accidental scratches and defects, on thermoplastic films.

#### Instead of Graphite

There is still no coal shortage, but the problem of graphite brushes for electric motors is known, surely, to many people. How often does repair of an electric razor or vacuum cleaner amount only to replacement of these same brushes. Unfortunately, brush-electrodes wear out quite fast, clogging up the motor with graphite dust in addition. Polymers from the polyacetylene series do not differ much in chemical composition from graphite. In a polyparadiethynylbenzene molecule,



two electronic clouds of polyacetylene chains are "sewn" by electronic clouds of phenyl rings. Such "massive cloudiness" leads, naturally, to high conductivity. This polymer has the record electrical conductivity:  $10^3 \text{ Ohm}^{-1} \text{ cm}^{-1}$ , and the width of its forbidden zone is less than 0.1 eV. This means that its electrical conductivity is approximately one order higher than that of graphite.

Electrically conducting tissue, which is pressed into resin, is prepared from such a polymer, and a composition is obtained which is entirely suitable for the production of mobile contacts. The production is almost without waste: the brush is immediately, upon pressing, given the necessary dimensions and forms. And these brushes last one order longer than graphite ones. Thus, graphite brushes in a trolley-bus motor must be changed every month (and also the motor collector must be cleared of graphite dust and oxidized copper), while polymer brushes can, without wearing out, last a year, and the collector then remains clean. (When fitting the brushes, a polymer film is formed on the collector, and the rubbing surfaces become as smooth as a mirror.)

Graphite in a trolley-bus still works at one spot, at the ends of rod-current-stripping devices. Contact with the wire is through graphite bearings. They operate under any conditions--in heat, cold, and, most importantly, during precipitation. The result is that in bad weather the bearings do not hold up for even one shift. Polymeric brushes, on the other hand, last 10 times longer under such conditions.

Graphite brushes spark, and as a result are a source of radio interference. It has long been known how it is possible in principle to lessen interference: the brushes must not be made solid, but assembled from plastic. In practice, it is not easy to do this: graphite crumbles and thin plastics fold up. A polymeric brush, though, is made of many fibers, divided by an insulator. Therefore, it does not spark and does not create radio interference. However, the unique structure of the polymeric brush also produces complications: for a reliable electrical contact of numerous fibers with the wire, the brush must be sewn with copper rivets.

Chemists believe that the high electrical conductivity of polyparadiethynylbenzene is not the end. The hope, to obtain polymers with even higher electrical conductivity, is based on theoretical and experimental research. How is one to know if, in time, wires will not appear with a core of polymer-conductor and a coating of polymer-insulator.

#### Instead of Silicon and Lead

The polymers which have already been discussed have preserved the family trait of the polyacetylene series--the system of conjugated bonds. But each of these "Crown Princes" has acquired its own traits, defining the spheres of its application. The "King" itself, polyacetylene, remained for a long time outside of things. However, several years ago, chemists of the University of Pennsylvania announced the creation of a solar battery and accumulator on the basis of polyacetylene. Not on its derivatives--but itself!

The first bri-f reports on these devices appeared in scientific and popular publications almost simultaneously. The tone of publicity announcements led one to believe that soon polyacetylene would replace silicon in solar batteries and lead in accumulators. However, in scientific publications, the style of which was, naturally, more reserved, and the conclusions more

cautious, only laboratory experiments were discussed, the goal of which was to demonstrate the effects and evaluate their value. Therefore, we shall refrain from broadcasting advertisements--only facts.

American chemists have learned to alloy polyacetylene--to substitute a portion of hydrogen ions in a polymeric chain by the necessary cations or to bring anions to them. Halogens served as acceptors, and alkali metals as donors. (Respectively, semiconductors of the p- and n- type were obtained; it is possible, in principle, to also make diodes out of polyacetylene.) The change in conductivity of the semiconductor when alloyed is a classic effect, but it is not manifested so clearly on any traditional semiconductor: during alloying, the black film of polyacetylene acquires a golden color and metallic shine, and its conductivity rises  $10^{12}$ -fold. Alloyed polyacetylene is sensitive to light, and this made it possible to construct a solar battery on its basis.

It is constructed very simply: two electrodes, polyacetylene and platinum, are submerged into the electrolyte--a sodium sulfide solution. A quantum of light generates electron-hole vapor in polyacetylene, and the electron is transmitted through the electrolyte to the platinum electrode--the current flows along the chain. Upon illumination, "approximately one Sun," the voltage for one polyacetylene battery was 0.3 volts, and the quantum effectiveness--1%. That means that only one quantum of light in 100 is operating. Characteristics of the usual silicon solar batteries are still significantly higher.

Now, on to the accumulator which was created by American chemists. Here, the reversibility of alloying comes into use. The accumulator has a polyacetylene cathode and a lithium anode; a  $\text{LiClO}_4$  solution serves as the electrolyte. Charging of the accumulator is done by alloying polyacetylene with  $\text{ClO}_4$ ;  $\text{Li}^+$  ions then proceed to the lithium anode. Upon accumulator discharge, all of these processes occur in reverse order.

Voltage of the accumulator is 3.7 V, but it is too early to judge the remaining characteristics. The accumulator was constructed in a flask, the dimensions of its electrodes are about a square centimeter and the power is low. And, of course, evaluations of specific characteristics--per kilogram of accumulator weight--cannot be precise as yet. The figures are reported as follows: density of accumulated energy 25  $\text{Vt/kg}$  (as much as for an automobile lead-acid battery), specific power 680  $\text{Vt/kg}$  (significantly higher than for ordinary accumulators).

This difference is explained by the structure of polymeric film: it consists of fibers with a diameter of around 200 Å, which fill up approximately one third of the volume. Therefore, polyethylene films have a highly effective surface. Consequently, the accumulator can charge and discharge very quickly. One disadvantage of the polyacetylene accumulator is obvious: it must be filled with inert gas and hermetically sealed, as contact with the air for both lithium and polyacetylene electrodes is inadmissible.

But, as they say, the first step is the hardest. Compared with its derivatives, polyacetylene still does not appear to be a patriarch, but more an infant. What will it become?

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12473

CSO: 1841/197

UDC 541.64:532.783:539.199

## LIQUID-CRYSTAL RIDGED POLYMERS IN ELECTRIC FIELD

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 5, Feb 84  
(manuscript received 1 Jun 83) pp 1149-1152

TAL'ROZE, R. V., SINITSYN, V. V., KOROBENIKOVA, I. A., SHIBAYEV, V. P. and PLATE, N. A., corresponding member, USSR Academy of Sciences, Moscow State University imeni M. V. Lomonosov

[Abstract] In recent years extensive study of thermotropic liquid crystal polymers has brought significant new developments concerning their properties in electric and magnetic fields. The present article reports on the orientation process of ridged liquid crystal polymers, focussing on process kinetics in nitrile-containing polymers with positive dielectric anisotropy. Data reveal a linear nature in the negative relationship of orientation time to the square of tension magnitude, indicating that like low-molecular liquid crystals, the orientation process in the tested liquid crystals is a function of dielectric reaction with the external field. Kinetic curves reflect a relaxational process, and the activation energy is practically independent of the degree of polymerization in numerous nematic polymers with identical mesogenous groups. The transition to polyacrylics had no practical impact on either orientation time or activation energy of the orientation process. Thus the key property is the anisotropy of dielectric permeability of the liquid crystal phase formed by side components of the macromolecule.

Figures 3; references 7: 5 Russian, 2 Western.

[187-12131]

UDC 542.951.8:547.721'495.1+547.723:546.268.2

## SYNTHESIS OF FURAN OLIGOURETHANES FROM 1-( $\alpha$ -FURYL)-2,2-DIMETHYL-1,3-PROPANEDIOL AND 2,4-TOLUYLENEDIISOCYANATE

Tashkent UZBEKSKIY KHMICHESKIY ZHURNAL in Russian No 1, Mar 84 (manuscript received 30 May 83) pp 56-58

SHAKIROV, F. M., MAGRUPOV, F. A. and ABSURASHIDOV, T. R., Tashkent Order of Peoples Friendship Polytechnic Institute imeni A. R. Beruni

[Abstract] Conditions are described for the synthesis of oligourethanes from 1-( $\alpha$ -furyl)-2,2-dimethyl-1,3-propanediol and 2,4-toluylenediisocyanate in chlorobenzene at elevated temperatures. At 373°K and a reaction time of  $2.16 \times 10^4$  sec the conversion rate was 55 percent, 80 percent at 393°K and 89 percent at 403°K. MW of the polymer was a function of the reaction time: at 403°K a reaction time of  $2.16 \times 10^4$  sec resulted in a polymer with a MW of 2700, while with a  $5.4 \times 10^4$  sec time a 8400 MW polymer was synthesized. Polymerization was markedly accelerated by the use of triethylamine as a catalyst. The oligourethanes were obtained as bright-yellow to dark-brown

powders, depending on the duration of polymerization, and were soluble at room temperature in monoethanolamine, dimethylformamide and cyclohexanone. Figures 2; references 8 (Russian).

[218-12172]

UDC 661.18.05+541.18.05

PREPARATION OF WATER-SOLUBLE POLYELECTROLYTE FROM POLYACRYLONITRILE POLYMER BY HYDRODYNAMIC APPARATUS

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Mar 84 (manuscript received 6 Jul 82) pp 19-23

KAMARYAN, S. G., KUSHCHEVA, L. Ye., AKHMEDOV, K. S. and ISKHAKOVA, K. M., Tashkent Order of Peoples Friendship Polytechnic Institute imeni Abu Raykhan Beruni

[Abstract] A DGDV-1 disperser was employed in inducing cavitation and vibrational perturbations in polyacrylonitrile (PAN) samples during hydrolysis in water or propanol, to evaluate the effects of such perturbations on the rate of hydrolysis. The studies were conducted at 90-95°C with a reagent ratio of PAN:NaOH:H<sub>2</sub>O equal to 1:0.4:8.6. In both water and propanol the rate of saponification was increased 2.5- to three-fold with a 12 min disperser treatment with an intensity of one cycle per 2 min. Polymers prepared by the use of the disperser showed a 10 percent decrease in mass loss on thermogravimetry, a 20°C increase in the temperature of decomposition, and a 6.4 kJ/mole increase in the energy of activation in destruction in comparison with polymers prepared without mechanical perturbations. Figures 2; references 9 (Russian).

[218-12172]

RADIATION CHEMISTRY

UDC 542.61:546.799.5

EXTRACTION OF AMERICIUM FROM ALKALINE SALT SOLUTIONS WITH ALKYL PYROCATECHIN

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript received 21 Oct 82) pp 21-24

KARALOVA, Z. K., RODIONOVA, L. M. and MYASOYEDOV, B. F.

[Abstract] In the process of plutonium-239 recovery, the tailings frequently contain significant quantities of plutonium and americium along with aluminum, iron, alkali and alkaline earth elements. These tailings must be reduced to a safe radioactive level before being discarded. In the present work, the feasibility of extracting americium directly from alkaline solutions high in salt content by using 4-( $\alpha,\alpha$ , dioxylethyl)-pyrocatechin (DOP) in the presence of DTPA and EDTA as complex forming ligands was studied. The method consists of adding 0.1 mole/liter of DOP in toluene to the test solution and conducting the extraction for 10 minutes at room temperature. The presence of isotopes still remaining in the solution was checked radiochemically. After a two-fold extraction, the solution had practically no radioactive isotopes in it. After regeneration with mineral acids, the extractant may be recycled. Figures 3; references 7: 5 Russian, 2 Western.

[193-83440972]

UDC 542.61:546.799.5

EXTRACTION OF AMERICIUM FROM ALKALINE SOLUTIONS WITH TECHNICAL MIXTURE OF MONO- AND DIDECYL PYROCATECHINS

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript received 15 Dec 82) pp 24-28

KARALOVA, Z. K., RODIONOVA, L. M., MYASOYEDOV, B. F. and KUZNETSOVA, V. S.

[Abstract] It was previously shown that only quaternary ammonium bases and 4-( $\alpha,\alpha$ -dioxylethyl)-pyrocatechin are capable of extracting transplutonium elements from alkaline solutions in the presence of complex forming ligands.

For the purpose of finding new and more readily available extractants, a study was made of the extraction of americium and europium in NaOH-DTPA using a mixture of mono- and didecylpyrocatechins (TAP) as extractants, the latter being more readily synthesized than the individual reagents. After determining the effects of various factors on the rate of americium extraction, optimal conditions were found. The rate of americium extraction was found to increase with increasing concentrations of alkali and extractant and decreasing concentrations of ligand and metal. In view of its simplicity of synthesis and its effective extracting and separating properties, it is concluded that TAP may be substituted for the less readily available individual alkylpyrocatechins. Figures 6; references 4: 3 Russian, 1 Western.

[193-83440972]

UDC 546.791:542.61:541.49

STUDY OF PROCESSES OF LIGAND EXCHANGE IN COMPLEXES OF URANYL WITH AMIDES OF PHOSPHORUS ACIDS IN AQUEOUS SOLUTIONS

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript received 27 Dec 82) pp 48-52

YAKSHIN, V. V., KHOKHLOVA, N. L., KAZAKOV, V. P. and AFONICHEV, D. D.

[Abstract] Special features of the P-N bond render phosphorus acid amides of the composition  $xP(O)(NR)_3$  more suitable than other organophosphorus extractants for both separation and extraction of actinoids from salt solutions. In the present work ligand exchange between uranyl complexes and the above phosphorus acid amides in aqueous solutions was studied using a photoluminescent technique. Bimolecular extinction coefficients were determined which characterized the rate of entry of the ligand into the coordination sphere. The effects of acidity, ionic strength and temperature of the solution on the deactivation processes were studied. These processes were found to follow a linear relationship with the free energy. Parameters were found which correlate the extinction coefficient to the reaction rate constant. It is hypothesized that an electron donor-acceptor relationship exists between the uranyl ion in the excited state and the phosphorus acid amide. The latter forms complexes with both the uranyl ion and with uranyl in the basic state. Figures 3; references 14: 12 Russian, 2 Western.

[193-83440972]

UDC 546.799.5/8

EXPERIMENTAL APPROACH TO CHEMICAL IDENTIFICATION OF ELEMENT 107 AS  
EKARHENIUM, PART 2: SEARCH FOR ISOTOPES OF ELEMENT 107 UNDERGOING SPON-  
TANEOUS FISSION IN REACTION PRODUCTS OF  $Bk^{249} + Ne^{22}$  USING THERMOCHROMATO-  
GRAPHIC METHOD

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript  
received 14 Sep 82) pp 76-80

ZVARA, I., DOMANOV, V. P., KHYUBENER, Z., SHALAYEVSKIY, M. R., TIMOKHIN,  
S. N., ZHUYKOV, B. L., AYKHLER, B. and BUKLANOV, G. V.

[Abstract] Having previously developed an express continuous thermochromato-  
graphic method for the separation of radioactive rhenium from mixtures of  
radioactive isotopes formed in nuclear reactors, an attempt was made to use  
a chemical means to separate any possible isotopes of element 107 from other  
elements undergoing spontaneous fission that are formed during irradiation  
of  $Bk^{249}$  with fast  $Ne^{22}$  ions. Spontaneous fission was recorded on a quartz  
tracking detector in the column. No tracks of spontaneous fission were  
detected, although the sensitivity of the experiment for isotopes having a  
half-life period of  $2-5 \cdot 10^4$  seconds was  $10^{-34} \text{ cm}^2$ . Figures 2; references  
10: 7 Russian, 3 Western.

[193-83440972]

UDC 542.943+546.799.4

REDUCTION OF PLUTONIUM (VI) IN NITRIC ACID SOLUTIONS UNDER  $\alpha$ -RADIATION

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript  
received 25 May 83) pp 94-98

ANDREYCHUK, N. N., ROTMANOV, K. V., FROLOV, A. A. and VASIL'YEV, V. Ya.

[Abstract] Results are presented of a systematic study of the radiation-  
chemical reduction of plutonium (VI) in nitric acid solutions of 0.3-6  
moles/liter concentration and 5-50 mmoles/liter plutonium (VI) concentration  
and 1-10 watts  $\alpha$ -radiation from a curium-244 source. The relationships of  
maximum reduction rate and induction period to concentrations of nitric  
acid, hydrogen ions, nitrate ions, plutonium (VI) and plutonium (IV), and  
dosage strength were established. At 0.3 mole/liter nitric acid concentra-  
tion, partial reduction of plutonium (VI) to (V) and (IV) to (III) take  
place. The induction period on the kinetic curves for plutonium (VI)  
reduction is governed by the  $PuVI \rightleftharpoons PuV$  equilibrium. Qualitative kinetic  
curves for plutonium (VI) reduction, as calculated by computer, agree favor-  
ably with experimental curves. Figures 4; references 13: 111 Russian, 2  
Western.

[193-83440972]

UDC 543.06:541.451

COMBINED METHOD FOR DETERMINING ATOMIC RATIO OF OXYGEN TO METAL IN MIXED OXIDE URANIUM-PLUTONIUM FUEL

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript received 25 May 83) pp 133-137

KOROLEV, S. I., KUPERMAN, A. Ya. and MUKHORTOV, N. F.

[Abstract] The oxygen coefficient, i.e., the atomic ratio of oxygen to metal ( $O/U+Pu$ ), has a great bearing on the physical-chemical, thermophysical and mechanical properties of mixed oxide nuclear fuels, and is therefore an important indicator of its quality. Many methods have been proposed to determine this quantity, but they all have drawbacks. In the present work, the authors modified what to them appeared to be the most promising. Specifically, a 100-300 mg sample is weighed and placed into a quartz tube containing 5 ml of 96 percent phosphoric acid. Through a special side opening, a solution of sodium chloride is injected to displace the air which is evacuated with a pump and replaced with argon. The tube is then heated to 330°C to dissolve the sample. After cooling, an aliquot of one  $cm^3$  is withdrawn and analyzed chromatographically. Hydrogen content is determined by the height of the corresponding peak. Knowing the total volume of the system and the hydrogen content in the aliquot, its total content in the gas phase can be calculated. After determining the uranium (IV) and plutonium (III) contents coulombometrically, the oxygen coefficient can be computed by formula. Figures 1; references 6: 1 Russian, 5 Western.

[193-83440972]

UDC 546.799.3:54677945:542.928

METHOD FOR DEEP PURIFICATION OF NEPTUNIUM FROM MICRO ADMIXTURES OF PLUTONIUM

Leningrad RADIOKHIMIYA in Russian Vol 26, No 1, Jan-Feb 84 (manuscript received 13 Dec 82) pp 138-140

TANANAYEV, I. G., DZYUBENKO, V. I. and KROT, N. N.

[Abstract] High purity neptunium is frequently required in research problems, but the current methods for preparing it, especially the separation from plutonium, are unsatisfactory. The authors have developed a new anion exchange method for separating neptunium from micro quantities of plutonium that is based on reduction elution of plutonium from a sorbent layer with a solution of hydroquinone hydrochloride. Neptunium obtained by this method contains less than  $3 \cdot 10^{-5}\%$  by weight of plutonium. References 5: 1 Russian, 4 Western.

[193-83440972]

UDC 666.192:546.18

MECHANISMS OF POST-RADIATION TRANSFORMATIONS IN ALKALINE-PHOSPHATE GLASSES ACTIVATED BY COPPER

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 5, Feb 84 (manuscript received 17 Jun 83) pp 1117-1119

VIL'CHINSKAYA, N. N., DMITRYUK, A. V., IGNAT'YEV, Ye. G., KARAPETYAN, G. O. and PETROVSKIY, G. T., corresponding member, USSR Academy of Sciences, State Optics Institute imeni S. I. Vavilov, Leningrad

[Abstract] Radiation color centers in phosphate glasses have been studied by electron spin resonance and optic spectroscopy, with the result that  $\text{PO}_4^{2-}$  paramagnetic perforation centers were related to absorption in the visible spectrum. The present study reveals the complexity of the phenomenon by its discovery of selective decoloration of radiation color centers when  $\text{Cu}^{2+}$  ion-protectors are introduced into the glass. Lithium-aluminum-phosphate glasses were activated by 0 to 0.13 percent copper under reduction conditions to avoid bivalent copper in unirradiated glass samples. Decoloration was observed in both optic and ultra-high-frequency wave lengths. Further assessment indicated that copper oxidation was also a post-radiation effect that followed the cessation of radiation.  $\text{PO}_4^{2-}$  centers were a reservoir of perforations used in oxidation. With copper content above 0.1 percent, the redistribution of perforation between  $\text{PO}_4^{2-}$  and Cu(II) was the predominant process observed. The paramagnetic analog of the coloration center with maximum absorption at 410 nm was not discovered, but this point was the electron center of electron capture. Figure 1; references 5:

3 Russian, 2 Western.

[187-12131]

UDC 621.039.54:542.61:54-145.4

PHYSICOCHEMICAL BASES OF OPTIMIZING EXTRACTANT STRUCTURE FOR REGENERATING SPENT ATOMIC POWER PLANT FUEL

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 274, No 5, Feb 84 (manuscript received 20 Jun 83) pp 1139-1144

ROZEN, A. M., SHMIDT, V. S., NIKOLOTOVA, Z. I., KARTASHEVA, N. A. and NIKIFOROV, A. S., corresponding member, USSR Academy of Sciences, All-Union Scientific Research Institute for Inorganic Materials, Moscow

[Abstract] Improvement can be made in extraction systems based on tributyl-phosphate with hydrocarbon diluents by perfecting the latter or optimizing extractant phosphate (TBP), which can extract uranium and plutonium but is incompatible with certain actinides. The authors then present a theoretical approach based on using trialkylphosphates and improving physicochemical properties of extractants to vary the chain length of hydrocarbons.

Compatibility improvements and reduced solvency in water are outlined. Experimental tests confirmed the theoretical calculations and indicated that a synthetic acid  $(RO)_2POOH$  for symmetrical phosphates and  $(i-C_4H_9O)(i-C_8H_{17}O)POOH$  for DiBiOP were effective for purging oxidized impurities. TiAP and DiBiOP were as effective for purifying spent atomic power plant fuels as previously employed TBP. Figures 4; references 15: 10 Russian, 5 Western.

[187-12131]

UDC 546.11.027.3+547.898

#### MACROCYCLIC POLYESTERS, LABELED WITH TRITIUM

Moscow BIOORGANICHESKAYA KHIMIYA in Russian Vol 10, No 1, Jan 84 (manuscript received 5 Jul 83) pp 121-123

NEYMAN, L. A., ANTROPOVA, S. P., KONUP, I. P., CHEPELEV, V. M. and NAZAROV, Ye. I., Institute of Bioorganic Chemistry imeni M. M. Shemyakin, USSR Academy of Sciences, Moscow; Odessa Physical-Chemical Institute, Ukrainian SSR Academy of Sciences

[Abstract] Macroyclic polyesters, so-called crown esters, are membrane-active complexons and are used for selective extraction, homogenization of reaction mixtures, phase transition catalysts, and more recently, biological activity. However, existing problems of toxicology and pharmacokinetics remain unresolved due to a lack of tritium-labeled compounds of high specific radioactivity. In the present work, tritium-labeled cyclopolymers of excellent chemical and radiochemical activity were prepared by thermal activation of tritium gas. Figures 3; references 11: 6 Russian, 5 Western.

[142083440972]

RUBBER AND ELASTOMERS

UDC 547.1

EFFECT OF EMULSION POLYMERIZATION CONDITIONS ON PROPERTIES OF CARBOXYL-CONTAINING ACRYLIC COPOLYMER AND ITS LATEX

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 15 Aug 83) pp 7-8

KHAVKINA, B. L., RYZHOV, V. B. and ZAYTSEVA, N. A., Moscow Textile Institute imeni A. N. Kosygin

[Abstract] In studying the relationship between polymer structure and the colloidal chemical properties of the latex, difficulties arise due to comonomers varying in polarity, such as with carboxyl-containing acrylates. Electron microscope analysis fails to give the molecular structure and the composition of the copolymer. In the present work, five latex samples of varying combinations of butyl acrylate, methylmethacrylate and methacrylic acid were studied. Depending on the method of emulsion polymerization, the particle size of the latex changes. Thus, increasing the polymerization duration from 40 to 80 minutes decreases the particle size according to centrifugal sedimentation analysis. At the same time, however, electron microscope data show that the particles are identical in size. This contradiction may be due to a change in the interaction of the particles with the medium, and therefore the sedimentation capability. Turbidometric titration data show that the molecular structure of the latex polymer and the ratio of polar to nonpolar groups change in accordance to the method of synthesis.

Figures 1; references 4 (Russian).

[182-83440972]

UDC 678.664.074:678.4.048

## INTERACTION OF POLY(OXYHYDROXY)URETHANES WITH FILLERS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 9 Jun 83 pp 9-11

IONINA, N. V., TROSTYANSKAYA, I. I. and RAPPOPORT, L. Ya., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev

[Abstract] Elastic polyurethanes have been synthesized from oligomeric cyclocarbonates and diamines. These polyurethanes, in contrast to those prepared by the conventional isocynate method, have active hydroxyl side groups which are capable of association with a filler, such as white soot or aerosil, which also has chemically active hydroxyl groups. A study was made of the interaction of poly(oxyhydroxy)urethane with white soot U-333. Infra-red spectrum analysis shows that specific intermolecular polymer-filler bonds are formed between polyurethanes having hydroxyl groups and filler if the filler also has chemically bound hydroxyl groups. Figures 3; references 11 (Russian).

[182-83440972]

UDC 678.762.2:53

## FROST RESISTANCE OF VARIOUS BUTADIENE RUBBERS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 15 Dec 82) pp 11-13

NOVIKOVA, G. Ye., PANKRATOVA, Ye. D., KARLINA, I. A. and MONGAYT, Ye. Z., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev

[Abstract] Rubbers based on cis-1,4-polybutadiene have good low temperature characteristics because of the low glassification temperature of the polymer (-112°C), but a high content of 1,4-linkages results in crystallization so that butadiene is usually copolymerized with other monomers. The frost-resistant characteristic of six butadiene copolymers ranging from 35 to 96 percent 1,4-linkages are compared. As expected, the tendency towards crystallization increased with increasing purity of the microstructure. Study of the effects of the crystal phase on the mechanical properties showed that the rate of crystallization increases with increasing content of 1,4-linkages and Mooney viscosity. The study showed that rubber SKDP has the least tendency to crystallization, the highest frost resistance, and is equal to butadiene rubber of regular structure. References 6: 5 Russian, 1 Western.

[182-83440972]

INTERACTION OF FLUORO RUBBERS WITH CERTAIN ORGANIC LIQUIDS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 12 Sep 83) pp 13-14

LYTKINA, N. I., VANSYATSKAYA, L. N., MIZEROVSKIY, L. N. and SHCHEGLOVA, O. V., Ivanovsky Scientific Research Institute of Film Materials and Artificial Leather of Technical Grade

[Abstract] Fluoro rubbers are chemically inert and are widely used as corrosion resistant materials although quantitative data on their physical interaction with organic solvents is absent in the literature. Accordingly, a study was made of the interaction of SKF-26 and SKF-32 with various solvents. Equilibrium bulk swelling constants were determined for the two vulcanizates in 25 different solvents. The results show that the vulcanizates are resistant to aliphatic and aromatic hydrocarbons, their chlorine derivatives, alcohols and primary aromatic amines, but that they react vigorously with ketones, carboxylic acids, simple and mixed esters, tertiary amines and dimethylformamide. By substituting a chlorine atom for a  $CF_3$  group (SKF-32 instead of SKF-26), the affinity of the fluoro rubber to all studied solvents increases markedly. Figures 1; references 4 (Russian).

[182-83440972]

URETHANE VULCANIZING AGENTS AND VULCANIZATION ACCELERATORS FOR CHLOROPRENE RUBBER

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 12 Jan 83) pp 20-22

CHERENYUK, I. P. and AVDEYENKO, A. P., Siberian Technologic Institute and Kramatorsk Industrial Institute

[Abstract] Chloroprene rubbers vulcanized with quinonemonooximes are high in strength, resistance to thermal aging, wear and other properties. A study was made of the possibility of using urethanes in polychloroprene rubber mixtures. However, urethanes obtained from quinonemonooximes cause rapid subvulcanization so that other compounds obtained by reaction of *p*-quinonemonooxime with various isocyanates must be used. Vulcanization tests were run with quinonemonooxime, monophenylurethanes, monoallylurethane, 2,4-toluylenediisocynate and its dimer, diethyleneglycolurethane, tri-isocyanate and polyisocyanate as vulcanizing agents. Optimum vulcanization duration at 143°C was 50 minutes for all mixtures, although the resistance to subvulcanization was found to depend on the composition of the agent. The tests showed that quinonedioxime-based urethanes may be used in place of metal oxides as vulcanizing agents or accelerators. References 5: 3

2 Western.

[182-83440972]

UDC 678.746.3.043

USING AZOPEROXIDE TO OBTAIN POROUS RUBBERS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 25 Jul 83) pp 24-25

SOLOV'YEVA, G. A., KLOCHKOV, V. I., PECHNIKOV, M. S., and KRASOVSKIY, V. N., Leningrad Technologic Institute imeni Lensoviet; Leningrad Production Association "Krasnyy Treugol'nik"

[Abstract] A basic condition needed to obtain quality products from porous rubbers is the compatibility of the vulcanization and pore forming processes. This is made possible by using an organic pore former such as azoperoxide. Tests run on six rubbers showed that the effectiveness of pore formation is related to the vulcanizing activity of the azoperoxide, which appears to be more active for butadiene rubber and its copolymers than for polyisoprene. A study of azoperoxide vulcanizates with SKS-30ARKP rubber and comparison with sulfur vulcanizates showed that they have improved properties, e.g. less settling and residual deformation on compression at high temperatures. Thus, azoperoxide may be used to prepare porous rubbers from diene latexes. Figures 2; references 6 (Russian).

[182-83440972]

UDC 678.762.2-134:544.3.544

DETERMINING CONTENT OF BUTADIENE PIPERYLENE COPOLYMER BY PYROLYTIC GAS CHROMATOGRAPHY

Moscow KAUCHUK I REZINA in Russian No 2, Feb 84 (manuscript received 31 Mar 83) pp 33-34

YEVDOKIMOVA, S. P., DROZDOVA, E. V., NCVIKOVA, Zh. H. and SHISHKINA, K. L., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev

[Abstract] Butadiene-piperylene copolymers have physical and mechanical properties similar to polybutylene but have higher frost resistance owing to the presence of 8-12% piperlyene links in the macromolecule. To determine the copolymer composition, a technique was developed that is based on pyrolytic gas chromatography. The method is suitable for both laboratory and plant use. Figures 3; references 1 (Russian).

[182-83440972]

WATER TREATMENT

UDC 628.16.087

PRACTICAL UTILIZATION OF SEDIMENTS CONTAINING OXIDES OF HEAVY METALS

Kiev KHIMIYA I TEKHNOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 21 Sep 82) pp 35-37

MAKAROV, V. M., INDEYKIN, Ye. A., YUSOVA, A. P., SAVITSKAYA, I. V., BABANIN, V. F., VASIL'YEV, S. V. and DERBENEVA, L. G., Yaroslavl Polytechnic Institute

[Abstract] Waste effluent from electroplating shops is frequently subjected to electrocoagulation with steel electrodes to form ferric and ferrous hydroxides. By applying appropriate seeding techniques, the coagulant may be made to form brown iron oxide pigment and/or a ferromagnetic powder which may be used to make ferrite. Both products are at least equivalent in quality to the serially produced counterparts. Figures 1; references 7 (Russian).

[183-83440972]

UDC 541.183:628.33.162.8

COMBINED METHOD FOR TREATING WASTE WATERS CONTAMINATED WITH DYESTUFFS

Kiev KHIMIYA I TEKHNOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 6 Oct 82) pp 51-53

KOZHANOV, V. A., KLIMENKO, N. A., SID'KO, R. Ya. and KERZHNER, B. K., Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskii, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Not one of the presently known methods for removing dyestuffs from waste effluent is both universally satisfactory and economical. The present study shows that by combining the coagulation and ozonization steps at the decoloring stage of effluent treatment and by concentrating the pollutants and then varying the acidity of the solution, it is possible to recover the sludge and make the ozonization process more efficient. References 4: 3 Russian, 1 Western.

[183-83440972]

UDC 628.49.081.3

USE OF MAGNESIUM SALTS IN TECHNOLOGY OF WATER PURIFICATION FROM BASIC DYES

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 11 Oct 82) pp 53-56

KUL'SKIY, L. A., SHKAVRO, Z. N., MEDVEDEV, M. I. and ZUL'FIGAROV, O. S., Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A study was made to determine the effectiveness of water purification from various basic dyes by using magnesium salt hydrolyzates and to establish the effect of anionic composition of the precipitant on the process. Results showed that magnesium hydroxide can be used to remove basic dyes by hydrolysis in the presence of  $Na_2SiO_3$  and as precipitants by hydrolysis in the presence of calcium or sodium hydroxides and organomineral sorbents. Figures 5; references 14: 12 Russian, 2 Western.  
[183-83440972]

UDC 628.543

SEPARATION OF FLUORINE DURING WASTE WATER NEUTRALIZATION PROCESS IN PRODUCTION OF MINERAL FERTILIZERS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 10 Jun 82) pp 58-61

GAYEVOY, S. N., MISHIN, N. I. and DERGUNOVA, L. G., Scientific Research Institute for Fertilizers and Insectofungicides, Scientific Production Association "Minudobreniya", Voskresenskiy Branch

[Abstract] In the production of phosphate mineral fertilizers, large quantities of waste water are formed which contain phosphoric and fluosilicic acids. These effluents are currently neutralized with calcium hydroxide or carbonate and the calcium fluoride and phosphate residues are dumped. The present work was undertaken to study the effects of various factors on the precipitation of  $CaF_2$ , calcium phosphate and silicon dioxide and to determine the optimal conditions for treating the waste water for the purpose of recovering  $CaF_2$  for further refinement to fluorine compounds. It was found that the optimum conditions for fluorine removal are a pH of 3.0 - 3.2, calcium hydroxide as precipitant, and the presence of a flocculant. The precipitate must be washed to remove the phosphates. References 17: 12 Russian, 5 Western.  
[183-83440972]

UDC 621.359.7

ELECTROCHEMICAL PURIFICATION OF WASTE WATER FROM ORGANIC AND MINERAL SUBSTANCES

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 4 Aug 82) pp 64-66

SOBOLEVSKAYA, T. T., KHOROSHILOVA, O. N., KRIVORUCHKO, A. P., MAKHNO, A. G., GUDRIT, T. D. and GREBENYUK, V. D., Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] A study was made of the continuous purification of industrial effluent--containing some mineral mater, organic acids, alcohols and aldehydes--by anode oxidation and electrodialysis with a mixed layer of ionites in the desalination chamber of a four-chamber multipurpose electrodializer. Experiments showed that the optimum anode material is platinum with either activated charcoal PAV-SV or cationite KU-23ch as filler in the anode chamber. The desalination chamber should contain a mixed layer of KU-23ch and AV-17X9Pch in 1 : 1.4 ratio. Compared to acids, aldehydes and inorganic contaminants, alcohols are the most difficult to separate by electrodialysis and catalytic methods should be tried. Figures 1; references 9 (Russian). [183-83440972]

UDC 621.359.7

REMOVING HYDROCHLORIC ACID FROM WASTE EFFLUENT CONTAINING PRODUCTS OF ORGANIC SYNTHESIS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 22 Jun 82) pp 66-68

KONONOV, A. V., PONOMAREV, M. I., SHKARAPUTA, L. N., GREBENYUK, V. D. and SKLYAR, V. T., Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Department of Petrochemistry, Institute of Physical-Organic Chemistry and Coal Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] In the semicontinuous production of 3-chloro-4-oxysulfolan (chlorohydrin) the waste effluent contains hydrochloric acid and other organic substances. A study was made of the possibility of recovering and concentrating the hydrochloric acid by electrodialysis in a six-chamber laboratory dialyser with alternate MK-40 and MA-40 ion exchange membranes. The study showed that the presence of chlorohydrin and sulfolene has practically no deleterious effect on the electrochemical properties of the ion exchange membranes, and the compounds are carried over into the brine solution. Figures 3; references 4 (Russian). [183-83440972]

UDC 628.35

LOCAL BIOLOGICAL TREATMENT OF HIGHLY CONCENTRATED EFFLUENTS CONTAINING VOLATILE MATTER

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 27 Jul 82) pp 79-81

BYSTROV, G. A. and ZAYTSEVA, M. P., Okhtinskiy Scientific Production Association, "Plastpolimer", Leningrad

[Abstract] When spraying anticorrosive coatings of fluoroplastic materials, e.g., lacquers, emulsions, suspensions, water is used to form a mist screen to entrap the paint particles. The resulting effluent contains both polymeric matter as a gelatinous mass and dissolved matter. After filtration, there is still a large amount of harmful pollutants, 80 percent of which are volatile components and ammonia nitrogen. In the present work, an experimentally proved, four-stage scheme for local biological treatment is presented. It includes fermentation of the initial highly concentrated filtrate in a methane tank, precleaning of organic contaminants in an aeration tank followed by nitrification and denitrification to remove ammonia nitrogen. Water treated by this method satisfies the requirements for return to the reservoir or it may be recycled for anticorrosive coatings operation. Figures 3; references 3 (Russian).

[183-83440972]

UDC 628.165

CHANGE IN MICROBIAL CONTENT IN WATER WHILE MAKING IT POTABLE

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 1, Jan-Feb 84 (manuscript received 17 Nov 82) pp 86-88

KIL'SKIY, L. A., SAVLUK, O. S., VOLKONSKIY, V. A. and BAKHURSKAYA, L. P., Institute of Colloid Chemistry and Chemistry of Water imeni A. V. Dumanskiy, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Vacuum distillation of sea water at 40-60°C entails the possibility of bacteria surviving into the condensate. A laboratory scale study was made to determine the conditions under which microorganisms enter distilled water. Imitation sea water of 20 g/liter salt content was infested with *E. Coli* 1257, *Streptococcus faecalis*, *Bacillus subtilis*, *Staphylococcus aureus*, and *Bacillus mesentericus*. The data showed that vacuum distillation results in significant disinfection for all species of microorganisms, i.e., the disinfection is nonspecific. It depends greatly on the duration of the distillation. The study showed that vacuum distillation--with disinfectants added--of coastal sea water, often heavily contaminated, can result in potable water equivalent to GOST 2874-73. Figures 1; references 6: 5 Russian, 1 Western.

[183-83440972]

MISCELLANEOUS

UDC 541.14+541.124

PHOTOCHEMICAL REACTION OF TRIETHYLAMINE AND CHLOROFORM

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian No 1, Jan 84 (manuscript received 16 Feb 83) pp 51-52

MARKARYAN, Sh. A. and BEYLERIAN, N. M., Yerevan State University

[Abstract] Study of the photochemical reaction between triethylamine (TEA) and chloroform shows that it proceeds with dehydrogenation of TEA and with splitting off of a chlorine atom from the chloroform with formation of dichloromethane. Dichloromethane in a TEA-dichloromethane system also is subjected to dechlorination with the TEA acting as a dechlorinating agent in the liquid form and conversion of the halogenoalkanes into corresponding alkanes is possible. During study of reactions proceeding in systems with participation of TEA and a halogen-alkane solvent, the possibility of their interaction under the action of light must be considered. References 2 (Russian).

[216-2791]

CSO: 1841

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